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On Hayami's Turbulent Tensor

By

Toshizô Matsumoto

(Received January 20, 1942)

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1. On *Hydrological Studies on the Yangtze River, China*, Mr. Hayami[1] has introduced the following interesting turbulent tensor:

$$Y=C^2|\operatorname{rot}\boldsymbol{v}|\frac{(h^2-z^2)^2}{2(h^2+z^2)}\begin{pmatrix}0&0&0\\0&\frac{1}{2}&0\\0&0&1\end{pmatrix},$$

where the origin of the rectangular coordinate system is taken on the free surface (of the river, assumed flat), the x-axis in the direction of the flow (as that of the stream along the surface), while the z-axis is taken vertically downward.

According to Gebelein,[2] the turbulent tensor is

$$(1)\qquad \begin{cases} Y=C^2|\operatorname{rot}\boldsymbol{v}|\chi\begin{pmatrix}\frac{1}{2\varkappa}&0&0\\0&\frac{1}{2}&0\\0&0&\frac{1}{\varkappa+1}\end{pmatrix}, \\ \chi=z^2 \end{cases}$$

where the coordinate origin is taken on the boundary of the flow (the bottom of the river). This formula is applicable when the fluid fills the semi-infinite space on one side of the boundary surface. In applying this formula to the flow of the river whose free surface should be kept in its state, Mr. Hayami has imagined the virtual eddy of the true one at the bottom of the river, just symmetric with respect to the surface of the river. Then the turbulent tensor will be obtained by putting

$$\left\{\frac{1}{z^2}+\frac{1}{(2h-z)^2}\right\}^{-1}=\frac{z^2(2h-z)^2}{(2h-z)^2+z^2}$$

instead of z^2 in (1), where h is the depth of the river in consideration. Taking the coordinate origin on the free surface as stated above, we have

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1. Shôitirô Hayami, Hydrological Studies, IV. On the mechanics of flow in a wide river, Jour. Shanghai Sci. Inst., sec. I, vol. 1, No. 13 (1939).

2. H. Gebelein, Turbulenz (1935), p. 99.

$$(2)\qquad \begin{cases} Y = C^2 |\operatorname{rot} \boldsymbol{v}|\chi \begin{pmatrix} \frac{1}{2\varkappa} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{\varkappa+1} \end{pmatrix}, \\ \chi = \dfrac{(h^2-z^2)^2}{2(h^2+z^2)}. \end{cases}$$

Supposing h is constant, and the inclination j of the stream to the horisontal line is very small, so that $\sin j = j$, the equation of the steady, uniform with respect to x and non kinetically viscous turbulent motion is given by

$$(3)\qquad \frac{\partial}{\partial z}\left\{\eta_{zz}\frac{\partial u}{\partial z}\right\} = -gj,$$

where

$$(4)\qquad \eta_{zz} = C^2\chi\left|\frac{\partial u}{\partial z}\right|^{\frac{1}{\varkappa+1}} = C^2\frac{(h^2-z^2)^2}{2(h^2+z^2)}\left|\frac{\partial u}{\partial z}\right|^{\frac{1}{\varkappa+1}}.$$

Here u is the mean velocity in the x-direction. According to Mr. Hayami, $\varkappa$ is experimentally very nearly zero, so that we have instead of (4)

$$(5)\qquad \eta_{zz} = C^2\chi\left|\frac{\partial u}{\partial z}\right| = C^2\frac{(h^2-z^2)^2}{2(h^2+z^2)}\left|\frac{\partial u}{\partial z}\right|.$$

This is Mr. Hayami's component of the turbulent tensor.[1]

2. Let us remark that to keep the free surface in its natural state, only a virtual eddy is not sufficient. So we shall imagine an infinite number of virtual eddies at the vertical distances $\pm 2h$, $\pm 4h$,..... Considering the coordinate origin on the bottom of the river, put

$$(6)\qquad \begin{aligned} \frac{1}{\chi} &= \frac{1}{z^2} + \frac{1}{(2h-z)^2} + \frac{1}{(4h-z)^2} + \cdots\cdots \\ &\quad + \frac{1}{(-2h-z)^2} + \frac{1}{(-4h-z)^2} + \cdots\cdots \\ &= \sum_{n=-\infty}^{\infty} \frac{1}{(2nh-z)^2}. \end{aligned}$$

Then z^2 in Gebelein's turbulent tensor of (1) shall be replaced by the above χ.

Next we shall summate the series (6). As we know

$$\cot\vartheta = \frac{1}{\vartheta} + \sum_{n=-\infty}^{\infty}{}' \left(\frac{1}{\vartheta - n\pi} + \frac{1}{n\pi}\right);$$

whence we have

1. Here Gebelein, Loc. cit., p. 143 should be referred to.

$$(7) \qquad \operatorname{cosec}^2\vartheta=\sum_{n=-\infty}^{\infty}\frac{1}{(\vartheta-n\pi)^2}.$$

Therefore, comparing (6) and (7), we have

$$(8) \qquad \chi=\left(\frac{2h}{\pi}\right)^2\sin^2\frac{\pi z}{2h},$$

so that in the equation of the turbulent motion (3), we have to put instead of (5),

$$\eta_{zz}=C^2\chi\left|\frac{\partial u}{\partial z}\right|=C^2\left(\frac{2h}{\pi}\right)^2\sin^2\frac{\pi z}{2h}\left|\frac{\partial u}{\partial z}\right|.$$

Let us take the coordinate origin on the free surface and z-axis vertically downwards, then instead of the above formula, we have

$$(9) \qquad \eta_{zz}=C^2\chi\left|\frac{\partial u}{\partial z}\right|=C^2\left(\frac{2h}{\pi}\right)^2\cos^2\frac{\pi z}{2h}\left|\frac{\partial u}{\partial z}\right|.$$

Now integrating (3), we have (the tangential traction being zero),

$$\eta_{zz}\frac{\partial u}{\partial z}=-gjz.$$

Substituting the value of (9), we have

$$(10) \qquad \frac{\partial u}{\partial z}=-\frac{\sqrt{gjz}}{C\sqrt{\chi}}=-\frac{\sqrt{gjz}}{C\frac{2h}{\pi}\cos\frac{\pi z}{2h}}.$$

Changing the variable by

$$(11) \qquad z=h\zeta,$$

we have

$$(12) \qquad \frac{\partial u}{\partial\zeta}=-\frac{\pi\sqrt{gjh}}{2C}\frac{\sqrt{\zeta}}{\cos\frac{\pi}{2}\zeta},$$

where the ζ-axis directs vertically downwards and $\zeta=0$ on the free surface, while $\zeta=1$ at the bottom of the river. By (9) and (10), we have

$$(13) \qquad \eta_{zz}=C\sqrt{gjz}\,\sqrt{\chi}=\frac{2Ch\sqrt{gjh}}{\pi}\sqrt{\zeta}\cos\frac{\pi}{2}\zeta.$$

We shall put, as Mr. Hayami did,

$$(14) \qquad \Psi(\zeta)=\sqrt{\zeta}\cos\frac{\pi}{2}\zeta.$$

Then

$$(15) \qquad \eta_{zz}=\frac{2Ch\sqrt{gjh}}{\pi}\Psi(\zeta).$$

To find the maximum point ζ_0 of $\Psi(\zeta)$, we have to solve

$$\Psi'(\zeta)=\frac{1}{2\sqrt{\zeta}}\left(\cos\frac{\pi}{2}\zeta-\pi\zeta\sin\frac{\pi}{2}\zeta\right)=0.$$

Or putting $\frac{\pi}{2}\zeta_0=x_0$, we have

$$1-2x_0\tan x_0=0.$$

By the table and some simple calculations, we have (in comparison, Hayami's values[1] are written in the parenthesis)

$$x_0\fallingdotseq 0.6525,\ \zeta_0\fallingdotseq 0.415\ (0.40),\ \Psi(\zeta_0)\div 0.5121\ (0.4933)$$

Next $\int_0^1\Psi(\zeta)d\zeta\fallingdotseq 0.35739\ (0.3633,\ 0.3666)$;

hence the mean is attained at

$$\zeta_1\fallingdotseq 0.133\ (0.14),\qquad \zeta_2\fallingdotseq 0.724\ (0.68)$$

Table of $\Psi(\zeta)=\sqrt{\zeta}\cos\frac{\pi}{2}\zeta^2$

ζ	$\sqrt{\zeta}$	$\cos\frac{\pi}{2}\zeta$	$\sqrt{\zeta}\cos\frac{\pi}{2}\zeta$	Diff.
0.00	0.00000000	1.0000000	0.0000	0.1000
0.01	0.10000000	0.9998766	0.1000	0.0413
0.02	0.14142136	0.9995066	0.1413	0.0317
0.03	0.17320508	0.9988899	0.1730	0.0266
0.04	0.20000000	0.9980267	0.1996	0.0233
0.05	0.22360680	0.9969173	0.2229	0.0210
0.06	0.24494897	0.9955620	0.2439	0.0191
0.07	0.26457513	0.9939610	0.2630	0.0176
0.08	0.28284271	0.9921147	0.2806	0.0164
0.09	0.30000000	0.9900237	0.2970	0.0153
0.10	0.31622777	0.9876883	0.3123	0.0145
0.11	0.33166248	0.9851093	0.3268	0.0135
0.12	0.34641016	0.9822873	0.3403	0.0128
0.13	0.36055513	0.9792228	0.3531	0.0121
0.14	0.37416574	0.9759168	0.3652	0.0114
0.15	0.38729833	0.9723699	0.3766	0.0108
0.16	0.40000000	0.9685832	0.3874	0.0103
0.17	0.41231056	0.9645574	0.3977	0.0098
0.18	0.42426407	0.9602937	0.4075	0.0091
0.19	0.43588989	0.9557930	0.4166	0.0087
0.20	0.44721360	0.9510565	0.4253	0.0083
0.21	0.45825757	0.9460854	0.4336	0.0077

1. Hayami, Loc. cit., p. 245.
2. These calculalions we owe to Mr. Hirosi Nakahata. Thanks are due to him.

ζ	$\sqrt{\zeta}$	$\cos\frac{\pi}{2}\zeta$	$\sqrt{\zeta}\cos\frac{\pi}{2}\zeta$	Diff.
0.22	0.46904158	0.9408808	0.4413	0.0073
0.23	0.47958315	0.9354440	0.4486	0.0069
0.24	0.48989795	0.9297765	0.4555	0.0065
0.25	0.50000000	0.9238795	0.4620	0.0060
0.26	0.50990195	0.9177546	0.4680	0.0056
0.27	0.51961524	0.9114033	0.4736	0.0052
0.28	0.52915026	0.9048271	0.4788	0.0048
0.29	0.53851648	0.8980276	0.4836	0.0044
0.30	0.54772256	0.8910065	0.4880	0.0041
0.31	0.55677644	0.8837656	0.4921	0.0036
0.32	0.56568542	0.8763067	0.4957	0.0033
0.33	0.57445626	0.8686315	0.4990	0.0029
0.34	0.58309519	0.8607420	0.5019	0.0025
0.35	0.59160798	0.8526402	0.5044	0.0022
0.36	0.60000000	0.8443279	0.5066	0.0018
0.37	0.60827625	0.8358074	0.5084	0.0014
0.38	0.61644140	0.8270806	0.5098	0.0012
0.39	0.62449980	0.8181497	0.5110	0.0007
0.40	0.63245553	0.8090170	0.5117	0.0004
0.41	0.64031242	0.7996847	0.5121	**0.5121**
0.42	0.64807407	0.7901550	0.5121	**0.5121**
0.43	0.65574385	0.7804304	0.5117	0.0004
0.44	0.66332496	0.7705132	0.5111	0.0006
0.45	0.67082039	0.7604060	0.5101	0.0010
0.46	0.67823300	0.7501111	0.5087	0.0014
0.47	0.68556546	0.7396311	0.5071	0.0016
0.48	0.69282032	0.7289686	0.5051	0.0020
0.49	0.70000000	0.7181263	0.5027	0.0024
0.50	0.70710678	0.7071068	0.5000	0.0027
0.51	0.71414284	0.6959128	0.4969	0.0031
0.52	0.72111026	0.6845471	0.4936	0.0033
0.53	0.72801099	0.6730125	0.4899	0.0037
0.54	0.73484692	0.6613119	0.4860	0.0039
0.55	0.74161985	0.6494480	0.4817	0.0043
0.56	0.74833148	0.6374240	0.4770	0.0047
0.57	0.75498344	0.6252427	0.4719	0.0051
0.58	0.76157731	0.6129071	0.4668	0.0051
0.59	0.76811457	0.6004202	0.4612	0.0056

ζ	$\sqrt{\zeta}$	$\cos\frac{\pi}{2}\zeta$	$\sqrt{\zeta}\cos\frac{\pi}{2}\zeta$	Diff.
0.60	0.77459667	0.5877853	0.4553	0.0059
0.61	0.78102497	0.5750053	0.4491	0.0062
0.62	0.78740079	0.5620834	0.4426	0.0065
0.63	0.79372539	0.5490228	0.4357	0.0069
0.64	0.80000000	0.5358268	0.4286	0.0071
0.65	0.80622577	0.5224986	0.4212	0.0074
0.66	0.81240384	0.5090414	0.4135	0.0077
0.67	0.81853528	0.4954587	0.4056	0.0079
0.68	0.82462113	0.4817537	0.3973	0.0083
0.69	0.83066239	0.4679298	0.3888	0.0085
0.70	0.83666003	0.4539905	0.3799	0.0089
0.71	0.84261498	0.4399392	0.3707	0.0092
0.72	0.84852814	0.4257793	0.3613	0.0094
0.73	0.85440037	0.4115144	0.3516	0.0097
0.74	0.86023253	0.3971479	0.3417	0.0099
0.75	0.86602540	0.3826834	0.3314	0.0103
0.76	0.87177979	0.3681246	0.3209	0.0105
0.77	0.87749644	0.3534748	0.3102	0.0107
0.78	0.88317609	0.3387379	0.2991	0.0111
0.79	0.88881944	0.3239174	0.2879	0.0112
0.80	0.89442719	0.3090170	0.2764	0.0115
0.81	0.90000000	0.2940403	0.2646	0.0118
0.82	0.90553851	0.2789911	0.2526	0.0120
0.83	0.91104336	0.2638731	0.2404	0.0122
0.84	0.91651514	0.2486899	0.2279	0.0125
0.85	0.92195445	0.2334454	0.2153	0.0126
0.86	0.92736185	0.2181432	0.2023	0.0130
0.87	0.93273791	0.2027873	0.1892	0.0131
0.88	0.93808315	0.1873813	0.1758	0.0134
0.89	0.94339811	0.1719291	0.1622	0.0136
0.90	0.94868330	0.1564345	0.1484	0.0138
0.91	0.95393920	0.1409012	0.1344	0.0140
0.92	0.95916630	0.1253332	0.1202	0.0142
0.93	0.96436508	0.1097343	0.1058	0.0144
0.94	0.96953597	0.0941083	0.0912	0.0146
0.95	0.97467943	0.0784591	0.0765	0.0147
0.96	0.97979590	0.0627905	0.0615	0.0150

ζ	$\sqrt{\zeta}$	$\cos\frac{\pi}{2}\zeta$	$\sqrt{\zeta}\cos\frac{\pi}{2}\zeta$	Diff.
0.97	0.98488578	0.0471065	0.0464	0.0151
0.98	0.98994949	0.0314108	0.0311	0.0153
0.99	0.99498744	0.0157073	0.0156	0.0155
1.00	1.00000000	0.0000000	0.0000	0.0156
			35.7396	

The graph of the function is very similar to that of Mr. Hayami.[1]

3. Instead of (9), if we take Mr. Hayami's value (5), then we have

$$\Psi(\zeta)=\frac{(1-\zeta^2)\sqrt{\zeta}}{\sqrt{1+\zeta^2}}. \tag{16}$$

He has considered that this function is approximately near to the well known empirical formula:

$$\Psi(\zeta)=\zeta(1-\zeta). \tag{17}$$

In our case it will not be too rough if we approximate the sine curve of $\cos\frac{\pi}{2}\zeta$ by the parabolic arc of $1-\zeta^2$. Then we have from (14),

$$\Psi(\zeta)=\sqrt{\zeta}(1-\zeta^2). \tag{18}$$

In this case the equation (12) becomes

$$\frac{\partial u}{\partial\zeta}=-\frac{\pi\sqrt{gjh}}{2C}\frac{\sqrt{\zeta}}{1-\zeta^2}.$$

Hence

$$u=u_0+\frac{\pi\sqrt{gjh}}{2C}\left(\arctan\sqrt{\zeta}-\frac{1}{2}\log\frac{1+\sqrt{\zeta}}{1-\sqrt{\zeta}}\right). \tag{19}$$

Or expanding into the series,

$$\arctan\sqrt{\zeta}=\sqrt{\zeta}-\frac{\sqrt{\zeta}^3}{3}+\frac{\sqrt{\zeta}^5}{5}-\cdots\cdots,$$

$$\log\frac{1+\sqrt{\zeta}}{1-\sqrt{\zeta}}=2\left(\sqrt{\zeta}+\frac{\sqrt{\zeta}^3}{3}+\frac{\sqrt{\zeta}^5}{5}+\cdots\cdots\right),$$

$$(0\leqslant\zeta<1)$$

we have

$$u=u_0-\frac{\pi\sqrt{gjh}}{C}\sqrt{\zeta}^3\left(\frac{1}{3}+\frac{\zeta^2}{7}+\cdots\cdots\right). \tag{20}$$

1. Hayami, Loc. cit., p. 246.

This gives the vertical distribution of the velocity.

4. To study the bed of the river, we shall now consider the suspension of the matter in the river.[1] Let θ be the concentration of the suspended matter (weight of the matter per unit volume). Then

$$\frac{\partial}{\partial z}\left(\eta_{xz}\frac{\partial\theta}{\partial z}\right)=w_0\frac{\partial\theta}{\partial z}, \tag{21}$$

where w_0 is the setting velocity of the suspended particle and the coordinate system is taken as the above. Then integrating we have

$$\eta_{zz}\frac{\partial\theta}{\partial z}=w_0\theta+A,$$

where A is the integrating constant. Writing θ instead of $\theta+\frac{A}{w_0}$, we have

$$\eta_{zz}\frac{\partial\theta}{\partial z}=w_0\theta \quad \text{or} \quad \eta_{zz}\frac{\partial\theta}{\partial\zeta}=w_0h\theta.$$

Hence by aid of (15),

$$\log\frac{\theta}{\theta_0}=-w_0h\int_\zeta^{\zeta_0}\frac{d\zeta}{\eta_{zz}}=-\frac{\pi w_0}{2C\sqrt{gjh}}\int_\zeta^{\zeta_0}\frac{d\zeta}{\Psi(\zeta)}.$$

We cannot take $\zeta_0=1$, since then the improper integral does not exist. According to Mr. Hayami[2]

$$\zeta_0=0.9999.$$

Put

$$\Omega(\zeta)=\int_\zeta^{\zeta_0}\frac{d\zeta}{\Psi(\zeta)}=\int_\zeta^{\zeta_0}\frac{d\zeta}{\sqrt{\zeta}(1-\zeta^2)}. \tag{22}$$

Then we have

$$\Omega(\zeta)=\arctan\sqrt{\zeta}+\frac{1}{2}\log\frac{1+\sqrt{\zeta}}{1-\sqrt{\zeta}}\Bigg|_\zeta^{\zeta_0}.$$

Therefore

$$\log\frac{\theta}{\theta_0}=-\frac{\pi w_0}{2C\sqrt{gjh}}\Omega(\zeta) \tag{23}$$

$$=-\frac{\pi w_0}{2C\sqrt{gjh}}\left[\arctan\sqrt{\zeta}+\frac{1}{2}\log\frac{1+\sqrt{\zeta}}{1-\sqrt{\zeta}}\right]_\zeta^{\zeta_0}.$$

Using Mr. Hayami's data,[3]

$$\theta_0=10^5\text{g/cm}^3,\quad \frac{\theta}{\theta_0}=10^{-5},\quad C=0.2,\quad (\log_{10}e=0.4343)$$

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1. Hayami, Loc. cit., p. 253.
2. Hayami, Loc. cit., VII. On the stability of an erodible river bed with special reference to the lower Yangtze River. Jour. Shanghai Sci. Inst. New Series vol. 1, No. 1 (1941).
3. Hayami, Loc. eit., VII, p. 47.

we have by (23),

$$\frac{0.4343\pi}{2\times 0.2}\,\frac{w_0}{\sqrt{gjh}}\,\Omega(\zeta)=5. \tag{24}$$

From this equation we may find ζ corresponding to several values of

$$s=\frac{w_0}{\sqrt{gjh}}.$$

We have to solve the equation with respect to ζ:

$$\Omega(\zeta)=\frac{K}{s},\quad \left(K=\frac{5\times 2\times 0.2}{0.4343\pi}\fallingdotseq 1.48125\right) \tag{25}$$

into the form

$$\zeta=f(s). \tag{26}$$

The graph of this function has the shape of the integral sign. In Hayumi's case, the abrupt increase occurs between $s=0.2$ and 0.3.[1] In our case it occurs between $s=0.3$ and 0.4 as the following calculations[2] show.

$$\zeta_0=0.9999$$

$$\arctan\sqrt{\zeta_0}+\frac{1}{2}\log\frac{1+\sqrt{\zeta_0}}{1-\sqrt{\zeta_0}}\fallingdotseq 5.7363$$

i. When $s=0.3$ we have

$$\frac{K}{s}\fallingdotseq 4.9375.$$

Hence we have to solve

$$\arctan\sqrt{\zeta}+\frac{1}{2}\log\frac{1+\sqrt{\zeta}}{1-\sqrt{\zeta}}=0.7988$$

But for $\zeta=0.16$, „ „ $=0.8038$

$=0.15$, $=0.7775$

0.01, 0.0263

Hence $\zeta\fallingdotseq 0.1581$

ii. When $s=0.4$ we have

$$\frac{K}{s}\fallingdotseq 3.664$$

Hence we have to solve

$$\arctan\sqrt{\zeta}+\frac{1}{2}\log\frac{1+\sqrt{\zeta}}{1-\sqrt{\zeta}}=2.0699$$

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1. Hayami, Loc. cit., VII, p. 48.
2. We owe these to Mr. Keniti Koseki. Thanks are due to him.

But for $\zeta=0.77$, „ „ $=2.0840$
$=0.76$, $=2.0566$
0.01, 0.0274

Hence $\zeta\fallingdotseq\mathbf{0.7648}$

Thus we see the abrupt increase of $f(s)$ occurs between $s=0.3$ and 0.4. Moreover $f(0.26)\fallingdotseq 0$.

5. We remark that the graph of the function $\zeta=f(s)$ is of the shape of Γ, is common to all the improper integrals which are not convergent.

Let the integral be

$$\Omega(\zeta)=\int_{\zeta}^{\zeta_0}\frac{d\zeta}{\Psi(\zeta)} \quad \text{and} \quad \int_{\zeta}^{1}\frac{d\zeta}{\Psi(\zeta)}=\infty,$$

where

$$\Psi(\zeta)>0, \qquad \Psi(1)=0.$$

The function $\zeta=f(s)$ should change abruptly in an interval, say (a, b). It must be noted that the position of this interval in $(0, 1)$ depends upon the value of ζ_0. The interval (a, b) displaces in the direction of $s>0$, provided ζ_0 be taken nearer to $\zeta=1$.

For ζ_1 near to ζ_0, we have

$$\int_{\zeta}^{\zeta_0}\frac{d\zeta}{\Psi(\zeta)}=\frac{\zeta_0-\zeta}{\Psi(\bar{\zeta})}, \quad \zeta_1<\zeta<\bar{\zeta}<\zeta_0.$$

Hence by (25), we have

$$\frac{\zeta_0-\zeta}{\Psi(\zeta_1)}<\frac{K}{s}<\frac{\zeta_0-\zeta}{\Psi(\zeta_0)},$$

or

$$K\Psi(\zeta_0)<s(\zeta_0-\zeta)<K\Psi(\zeta_1),$$

wher $\Psi(\zeta)$ is supposed by hypothesis to decrease monotonously to zero. Therefore if we consider the hyperbolas

$$xy=K\Psi(\zeta_0)$$

and

$$x_1y=K\Psi(\zeta_1),$$

then we have for $y=\zeta_0-\zeta$, the inequalities

$$x<s<x_1,$$

i. e., s increases more rapidly than x of the first hyperbola, but slower than x_1 of the second one in $\zeta_1<\zeta<\zeta_0$. If ζ_0, ζ_1 are very near to 1, both hyperbolas turn very rapidly about their vertices. Therefore the Γ-form of $\zeta=f(s)$ becomes very aucute. Thus the rapid increase of $\zeta=f(s)$ in the neighbourhood of $\zeta=1$ depends upon the choice of the initial point ζ_0.

On the Pseudo-Photographic Effect of Coal and the Photographic Plates

By

Yaichiro Yamamoto

(Received March 24, 1942)

Abstract

The pseudo-photographic effect of coal was studied from the phenomena at the side of the plate. By using the KI-starch paper and the photographic plates, some properties of latent images induced by coal were observed. The pseudo-photographic sensitivity of photographic plates was also examined. It was found that the pseudo-photographic sensitivity seemed to be increased by the fog, and the photographic plates were sensitized by heating and light-exposure. The action of coal on the sensitized plates was analogous to that of H_2O_2. It may, therefore, be considered that the direct active agent in the coal is H_2O_2.

Coal has ability to affect a photographic plate in the dark. When the photographic plate is developed in the usual manner, a "contact photograph" is obtained which varies in character with the structure of the surface of the coal which is laid in contact with it. Such pseudo-photographic effect of coal has been studied by Halsam and Wheeler[1] and Ito.[2]

Recently, the writer has also been concerned in the study of this effect of coal in cooperation with H. Sawada and K. Morikawa.[3] There we studied the mechanism of this effect from the side of the coal and proposed the view that the peroxide (either H_2O_2 or O_3) which is formed during the oxidation of coal is the agent that affects the photographic plate.

In the present paper the author studies this effect from the side of the plate and compares the effect of coal with that of H_2O_2.

Preparation of Contact Photographs

To prepare contact photographs, the surface of a lump of coal is

1. G. S. Halsam and R. V. Wheeler: Fuel, **1**, 43, (1922). G. S. Halsam: Fuel, **7**, 253, (1928).
2. K. Ito: Bull. Inst. sci. Res. Manchukuo, **3**, 562, (1939).
3. H. Sawada, K. Morikawa and Y. Yamamoto: This will be published in J. Fuel Soc, (Japan).

polished by sand paper No. O; this surface is laid upon the film of a plate and heated during exposure at 30°C in a light-tight box in which humidity is kept at 79.5% by means of a saturated NH_4CL solution to accelerate the action of coal.

In the case of H_2O_2, a solution containing one part of commercial oxydol in 100 parts of water is used. 40 c.c. of this solution is measured into a glass crucible, and a plate is laid film-side down on the edge of the crucible, the film being 10 mm. apart from the liquid surface, and left in the dark at room temperature during 24 hours; then it is developed in the usual manner.

Investigation with KI-Starch Paper

In the previous investigation, when KI-starch paper was used instead of a photographic plate, a brown-violet iodine-starch figure was obtained on the paper which was identical with the normal contact photograph. When KI-starch paper was laid between the coal and the plate, the image on the plate was much weakened. From these facts, we proposed the view that the fogging agent in coal is absorbed by the KI-starch paper, that coal does not affect the plate directly, that the active agent is a peroxide (either H_2O_2 or O_3) which affects the KI-starch paper, and that H_2O_2 is more likely to be it than O_3.

The writer has now repeated this investigation. KI-starch paper was laid between coal and Ilford Process plate, and after a long exposure of 40 hours, the plate was carefully developed; in the region of the plate where the KI-starch paper was in contact with it, the image was not developed at the surface layer of the film, while at the deeper layer the image was clearly developed. Hence, by brief light exposure from the glass side of the plate, the image at the deeper layer is reprinted on the surface layer emulsion. Plate I, Fig. 1 (a) shows the contact photograph thus obtained, and Fig. 1 (b) in the same plate shows the iodine-starch figure on the KI-starch paper. This indicates that coal affects the KI-starch paper and the plate simultaneously, while the excess of iodine which is librated in the paper by coal diffuses into the film of the plate and diminishes the latent images at the surface layer. To confirm this diffusion of iodine, a plate exposed for a long time to coal through KI-starch paper is dipped in a 3% starch solution before development and after sufficient adsorption of the solution, it is dried in the dark room.

When it is taken out of the dark, no change is at first detectable

on the film, but gradually a violet figure proper to the iodine-starch reaction begins to appear and this figure is observed to be also identical to the normal contact photograph as shown in Plate I, Fig. 2 ; (a) showing the iodine-starch figure produced on the plate, (b) the normal contact photograph of the same sample. This shows first, that the excessive iodine which diffuses into the plate from the paper produces AgI by combination with silver that is liberated as latent image and diminishes the latent image at the surface layer of the film of the plate ; second, that when the plate is taken out to light, the photo-decomposition of AgI begins to take place, and iodine is again liberated and this time it reacts with the starch previously adsorbed in the film and shows the violet figure, as shown in Plate I, Fig. 2 (a).

Zinc also shows a very strong pseudo-photographic effect, but it does not affect KI-starch paper. The cause of the effect of zinc thus seems to be essentially different from that of coal. In the case of zinc, besides Russell's hydrogen peroxide theory,[1] it may be considered that atomic particles which are activated at the fresh metal surface affect a plate as proposed by S. Aoyama, T. Fukuroi and others.[2]

Different Kinds of Photographic Plates

The pseudo-photographic sensitivity for coal and H_2O_2 of the photographic plates and films used in this investigation is roughly shown in Table 1. The Fuji Al, Panchromatic and Process plates were new-

Table 1. Pseudo-photographic sensitivity of plates and films for coal and H_2O_2

	Coal	H_2O_2
Ilford Process plate	very strong	very strong
Ilford Special Rapid plate	strong	strong
Apem Noskrene	strong	strong
Kodak X-Ray film	strong	strong
Fuji X-Ray film	faint	faint
Fuji Al plate	faint	faint
Fuji Panchromatic plate	very faint	very faint
Fuji Process plate	non-sensitive	non-sensitive

1. W. J. Russell: Proc. Roy. Soc. London (A), **61**, 424, (1897); **63**, 102, (1898).

2. S. Aoyama, T. Fukuroi and I. Takahashi: Bull. I. P. C. R. (Tokyo), **12**, 493, (1933); **14**, 481, (1935). S. Aoyama, T. Fukuroi and N. Susuki: Bull. I. P. C. R. (Tokyo), **15**, 923, (1936).

ly purchased while the others have been stocked so long that they had sustained a natural ageing fog. The pseudo-photographic sensitivity in the case of coal and H_2O_2 seems to increase as the natural fog increases; namely, the primary silver which has been liberated as the natural fog in or very close to the so-called sensitivity specks of AgBr grains seems to operate as a necessary factor in the process of the action of coal and H_2O_2. If so, the removal of the primary silver will decrease the pseudo-photographic sensitivity of the plates. In order to remove the primary silver, a solution containing

5% $K_2Cr_2O_7$ solution	1 part
10-fold dilution of conc. HCL	2 parts
H_2O	15 parts

was used.

Ilford Process plates, which are most strongly fogged, are dipped in this solution for 15 sec. and washed with running water for one hour. Then their pseudo-photographic sensitivity for coal and H_2O_2 is found to have clearly decreased. As shown in Figs. 3 and 4 in Plate I, the action on the treated (right half) plates is weaker than on the untreated (left half) plates, because the primary silver has been transformed into AgCl by the reaction,

$$2Ag + K_2Cr_2O_7 + 2HCL \longrightarrow 2AgCl + \text{Reduction Products of } K_2Cr_2O_7,$$

and thereafter can not operate as the sensitizing factor.

Since the natural fog is stronger in the edge of the plate than in the central part, a certain amount of unchanged primary silver will remain, even after the treatment, in the edge in an amount proportional to the original fog. Hence, the desensitization effect of the solution must be weaker in the edge than in the central part. This tendency is apparent in Plate I, Fig. 3, in that the edge is used for treatment; on the treated plate from right (the central part of the original plate) to left (the edge part) the desensitization effect gradually decreases. Thus the primary silver in the fog acts as the necessary factor in the pseudo-photographic effect of coal and H_2O_2 and it thus sensitizes the plates.

Sensitization of Plates

Coal and H_2O_2 do not affect Fuji Process plates. If, however, plates are pseudo-photographic-sensitized by their natural fog as mentioned above, the artificial fog also should sensitize them. In order

to sensitize them, i. e., to give them the artificial fog, the writer has adopted the following methods which are often used in the usual sensitization of plates.

(a) By Heating

When a Fuji Process plate is heated at 40°C for two weeks, 8 hours a day, it is still not fogged, and so it is not sensitized for coal and H_2O_2. When it is heated at 55°C for 4—6 days, 8 hours a day, it is strongly fogged and becomes very pseudo-photographic-sensitive for coal and H_2O_2, as shown in Plate I, Fig. 5. In Fig. 5 the time of exposure is 29 hours, and the contact photograph was developed before the undesirable temperature fog appeared. The action on the plates heated for 6 days (left half) was stronger than that on those heated for 4 days (right half).

In the case of H_2O_2, it becomes so sensitive that the temperature fog is solarized. In this heating method, not only the silver liberated during the heating sensitizes the plate, but the relaxation of the gelatin film also allows a rapid penetration of the active agent in the coal through it.

(b) By Light-Exposure

When Fuji Process plate is light-exposed by a brown lamp (for the sensitive paper, 100V–10W) at a distance of 55 cm. for 5–10 sec., it also becomes pseudo-photographic-sensitive as shown in Plate I, Fig. 6, where the left half is exposed for 10 sec. and the right half for 5 sec. In this case, the sensitization effect is not so strong as in the case of heating.

According to Wightman and Quirk,[1] H_2O_2 intensifies the latent images before development, and the undevelopable latent images in the unintensified state are brought into the developable state owing to the reduction effect of H_2O_2; and AgBr grains with liberated primary silver in or very close to their sensitivity specks are very easily subject to the reduction effect of H_2O_2, because the reduction of the AgBr grains proceeds more easily from these silver-specks than from other points.

In the case of coal, the analogous intensification effect is detectable. The plate having the latent fog is pseudo-photographic-sensitive for coal just as mentioned above. In this case coal acts like H_2O_2 as the intensifier of the latent fog.

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1. E. P. Wightman and R. F. Quirk: J. Frank. Inst., **203**, 261, (1927); **204**, 731, (1927).

The plates, which are more or less developable owing to the natural or artificial fog, are also more pseudo-potographic-sensitive for coal. Therefore, the action of coal may be thought of as a kind of the intensification of the latent images, and H_2O_2 which is produced during the oxidation of coal seems to act as the intensifier. If O_3 is present, it will form H_2O_2 by combination with H_2O before acting on a plate, for the action of coal is accelerated by humidity and temperature as mentioned in the previous investigation.[1]

Consequently, the mechanism of the pseudo-photographic effect of coal at the plate side is the reduction of AgBr grains due to H_2O_2 which is the active agent in coal, and the reduction of AgBr grains by coal takes place easily when they are more or less developable due to certain factors.

In conclusion the writer wishes to express his sincere thanks to Professor U. Yoshida and Professor M. Miyata for their kindness and interest taken in this work. His hearty thanks are due to General Superintendent Dr. M. Sato, Mr. G. Okuno, Dr. K. Morikawa and Mr. H. Sawada for their kind encouragement throughout this work.

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1. loc. cit.,

Plate I

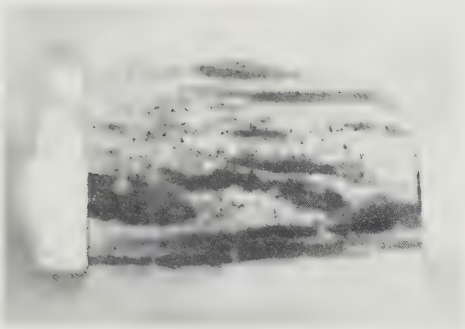

Fig. 1 (a)

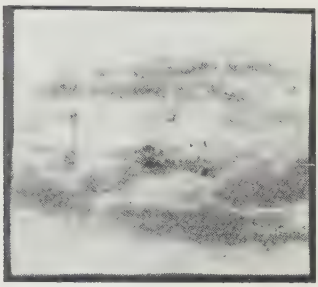

Fig. 1 (b)

Fig. 2 (a)

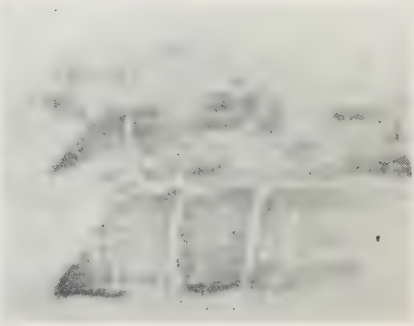

Fig. 2 (b)

Fig. 3

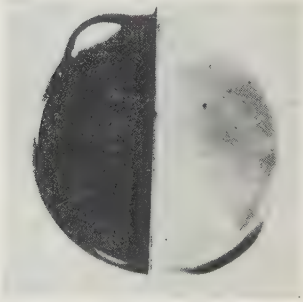

Fig. 4

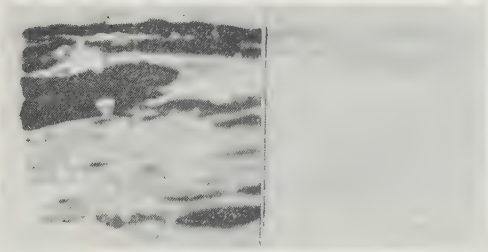

Fig. 5

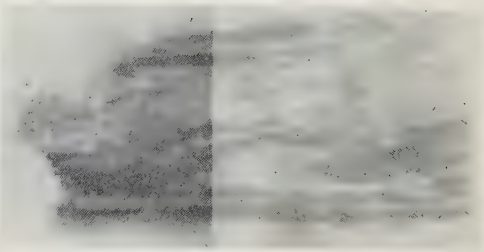

Fig. 6

A Note on Fowler's Differential Equation

By

Toshizô Matsumoto

(Received March 30, 1942)

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1. After G. Sansone,[1] Fowler's differential equation is

$$\frac{d}{d\xi}\left[\xi^2\frac{d\theta}{d\xi}\right]+\xi^\lambda\theta^n=0, \quad (\lambda>0,\ n\geqslant 0) \quad \ldots\ldots\ldots\ldots\ldots(1)$$

and its Emden's solution is such one that it satisfies the initial condition

$$\theta(+0)=C, \quad (0<C<\infty) \quad \ldots\ldots\ldots\ldots\ldots(2)$$

Emden[2] has studied the case $\lambda=2$ and Fowler[3] has continued the study for several cases. Sansone[1] has recently given a complete proof of the theorem in its general case: For that such a solution vanish at certain point of $0<\xi<\infty$, it is necessary and sufficient that $2\lambda-n+1>0$.

This number comes as a coefficient of an identity fundamental to his proof. But it would be impossible to perceive it at the first glance of the differential equation (1). The author intends to bring forward this number $2\lambda-n+1$ by the ordinary transformation of the differential equation.

After the differentiation, the equation (1) is

$$\xi\frac{d^2\theta}{d\xi^2}+2\frac{d\theta}{d\xi}+\xi^{\lambda-1}\theta^n=0 \quad \ldots\ldots\ldots\ldots\ldots(1')$$

By the substitution

$$\xi=e^{2u}, \quad u=\frac{1}{2}\log\xi \quad \ldots\ldots\ldots\ldots\ldots(3)$$

the equation becomes

$$\frac{d^2\theta}{du^2}+2\frac{d\theta}{du}+4e^{2\lambda u}\theta^n=0 \quad \ldots\ldots\ldots\ldots\ldots(4)$$

To have the differential equation without the term of the first order, we put as usual

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1. *Sulle soluzioni di Emden dell'equazione di Fowler;* Rendiconti di Matematica e delle sue applicazioni, **1** (1940), p. 163.
2. Gaskugeln, (1907).
3. Quartery Journ., **45** (1914); Ibid (Oxford series), **2** (1931).

$$\theta = ve^{-u}, \quad v = \theta e^{u}, \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

then the equation becomes

$$\frac{d^2v}{du^2} - v + 4e^{(2\lambda-n+1)u}v^n = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Here we see the number $2\lambda - n + 1$ which would play a special rôle.

2. To prove the necessity of the condition, Mr. Sansone has used the identity:

$$\frac{2\lambda-n+1}{2}\int_0^{\xi}\xi^2\left(\frac{d\theta}{d\xi}\right)^2 d\xi = \xi^{\lambda+1}\theta^{n+1}(\xi) + (\lambda+1)\xi^2\theta(\xi)\theta'(\xi) + \frac{n+1}{2}\xi^3\theta'^2(\xi) \ldots\ldots\ldots\ldots(7)$$

It is not explicitly remarked from what consideration he has derived it. For our equation (6), we derive it as follows:

From (6) we have

$$\left(\frac{d^2v}{du^2} - \frac{dv}{du}\right) + \left(\frac{dv}{du} - v\right) = -4e^{(2\lambda-n+1)u}v^n \ldots\ldots\ldots(6')$$

Multiplying both sides by $2\left(\frac{dv}{du} - v\right)$ and integrating, we have

$$\left(\frac{dv}{du} - v\right)^2 + 2\int\left(\frac{dv}{du} - v\right)^2 du = -8\int e^{(2\lambda-n+1)u}v^n\frac{dv}{du}du + 8\int e^{(2\lambda-n+1)u}v^{n+1}du + C.$$

If $n+1 \neq 0$ (for our case $n+1 \geqslant 0$), we have

$$\int e^{(2\lambda-n+1)u}v^n\frac{dv}{du}du = \frac{1}{n+1}\left\{e^{(2\lambda-n+1)u}v^{n+1} - (2\lambda-n+1)\int e^{(2\lambda-n+1)u}v^{n+1}du\right\}.$$

Hence

$$\left(\frac{dv}{du} - v\right)^2 + 2\int\left(\frac{dv}{du} - v\right)^2 du = -\frac{8}{n+1}e^{(2\lambda-n+1)u}v^{n+1} + \frac{16(\lambda+1)}{n+1}\int e^{(2\lambda-n+1)u}v^{n+1}du + C.$$

Now by (6)

$$4\int e^{(2\lambda-n+1)u}v^{n+1}du = \int\left(v - \frac{d^2v}{du^2}\right)v\,du = \int\left(v - \frac{dv}{du}\right)v\,du + \int\left(\frac{dv}{du} - \frac{d^2v}{du^2}\right)v\,du.$$

The second integral in the right is equal to

$$\left(v-\frac{dv}{du}\right)v-\int\left(v-\frac{dv}{du}\right)\frac{dv}{du}du$$
$$=\left(v-\frac{dv}{du}\right)v+\int\left(\frac{dv}{du}-v\right)^2du+\int\left(\frac{dv}{du}-v\right)v\,du.$$

Hence after a short calculation, we have

$$(2\lambda-n+1)\int\left(\frac{dv}{du}-v\right)^2du=4e^{(2\lambda-n+1)u}v^{n+1}+2(\lambda+1)\left(\frac{dv}{du}-v\right)v$$
$$+\frac{n+1}{2}\left(\frac{dv}{du}-v\right)^2+C'.$$

For $u\to-\infty$, v and $\frac{dv}{du}$ vanish and

$$e^{(2\lambda-n+1)u}v^{n+1}=e^{(2\lambda+1)u}v(ve^{-u})^n\to 0.$$

Hence $C'=0$ and the required identity for the equation (6) becomes

$$(2\lambda-n+1)\int_{-\infty}^{u}\left(\frac{dv}{du}-v\right)^2du=4e^{(2\lambda-n+1)u}v^{n+1}+2(\lambda+1)\left(\frac{dv}{du}-v\right)v$$
$$+\frac{n+1}{2}\left(\frac{dv}{du}-v\right)^2.\quad\ldots\ldots(8)$$

We remark that the identity may more easily be obtained provided $2\lambda-n+1\neq 0$. Multiplying both sides of the equation (6′) by v and integrating we have

$$\left(\frac{dv}{du}-v\right)v-\int\left(\frac{dv}{du}-v\right)\frac{dv}{du}du+\int\left(\frac{dv}{du}-v\right)v\,du$$
$$=-4\int e^{(2\lambda-n+1)u}v^{n+1}du.$$

Hence

$$\left(\frac{dv}{du}-v\right)v-\int\left(\frac{dv}{du}-v\right)^2du=-\frac{4}{2\lambda-n+1}e^{(2\lambda-n+1)u}v^{n+1}$$
$$+\frac{4(n+1)}{2\lambda-n+1}\int e^{(2\lambda-n+1)u}v^n\frac{dv}{du}du.$$

Observe that

$$4\int e^{(2\lambda-n+1)u}v^n\frac{dv}{du}du=\int\left(v-\frac{d^2v}{du^2}\right)\frac{dv}{du}du$$
$$=\frac{1}{2}v^2-\frac{1}{2}\left(\frac{dv}{du}\right)^2.$$

After a short calculation we shall have the identity.

L'inégalité nécessaire à la Théorie de la Classe Quasi-analytique de Fonctions de Deux Variables

Par

Sikazô Kodama

(Reçu en Avril 10, 1942)

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1. Si $g(u, v)$ est une fonction holomorphe dans les cercles fermés $|u| \leqslant 1$, $|v| \leqslant 1$, et s'annulant dans ces cercles ouverts, sans toutefois s'annuler aux origines, alors on peut, en désignant par u_0, v_0 les zéros de la fonction $g(u, v)$ par rapport à ses variables u, v, exprimer $g(u, v)$ dans le voisinage de (u_0, v_0) sous la forme suivante[1] :

$$g(u, v)=(u-u_0)^m(v-v_0)^{m'}\psi(u, v)\Omega(u, v), \tag{1. 1}$$

où

$$\begin{cases} \psi(u, v)=(u-u_0)^n+A_1(v)(u-u_0)^{n-1}+\cdots\cdots+A_n(v), \\ m,\ m',\ n \text{ sont les entiers positifs (ou nuls)}, \\ A_j(v)(j=1, 2, 3, \ldots, n) \text{ sont les fonctions holomorphes} \\ \text{s'annulant lorsque } v=v_0, \\ \Omega(u, v) \text{ est une fonction holomorphe ne s'annulant} \\ \text{pas dans ce voisinage.} \end{cases} \tag{1. 2}$$

Supposons, pour simplifier les idées, que l'égalité (1. 1) est réalisée dans tout le domaine. On a, par (5. 1)[2] de notre mémoire (I) p. 276, l'égalité suivante :

$$\log|\Omega(0, 0)| = \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\log|\Omega(e^{i\alpha}, e^{i\beta})|\,d\alpha d\beta \tag{1. 3}$$

$$= \frac{1}{4\pi^2}\int_0^{2\pi}d\beta\int_0^{2\pi}\log|\Omega(e^{i\alpha}, e^{i\beta})|\,d\alpha.$$

On tire de la

$$\log|g(0, 0)| - m\log|-u_0| - m'\log|-v_0| - \log|\psi(0, 0)| \tag{1. 4}$$

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1. Voir par exemple H. Behnke und P. Thullen: Theorie der Fuuktionen mehrerer komplexer Veränderlichen (1934), p. 57.

2. S. Kodama: Sur la Classe Quasi-analytique de Fonctions de Deux Variables (I) (Memoirs of the College of Science Kyoto Imperial University, Series A, Vol. XXII, 1939, p. 276).

$$= \frac{1}{4\pi^2}\int_0^{2\pi} d\beta \int_0^{2\pi} \{\log|g(e^{i\alpha}, e^{i\beta})| - m\log|e^{i\alpha}-u_0| - m'\log|e^{i\beta}-v_0| - \log|\psi(e^{i\alpha}, e^{i\beta})|\}\, d\alpha.$$

2. Posons

(2. 1) $\quad \psi(u, v)=(u-u_1)(u-u_2)\ldots(u-u_n),$

où $\quad u=Re^{i\alpha},\ v=re^{i\beta},\ |u|\leqslant 1,\ |v|\leqslant 1,\ u_j=R_je^{i\chi_j};$

et supposons que

$$(2.\ 2)\qquad \begin{cases} |u_j|<1 & (j=1,\ 2,\ldots,\ p), \\ |u_j|=1 & (j=p+1,\ p+2,\ldots,\ q), \\ |u_j|>1 & (j=q+1,\ q+2,\ldots,\ n). \end{cases}$$

Pour $u_j\neq 0$ $(j=1,\ 2,\ldots,\ p)$, on a, par la formule de Jensen,

$$(2.\ 3)\qquad \frac{1}{2\pi}\int_0^{2\pi}\log|u-u_j|\,d\alpha = \log|-u_j| + \log\frac{1}{|u_j|} = 0.$$

Pour $u_j=0$, on a

$$(2.\ 4)\qquad \frac{1}{2\pi}\int_0^{2\pi}\log|u-u_j|\,d\alpha = \frac{1}{2\pi}\int_0^{2\pi}\log R\,d\alpha\Big|_{R=1} = \log R\Big|_{R=1} = 0.$$

Pour $u_j (j=p+1,\ p+2,\ldots,\ q)$ (où $|u_j|=1$), on a

$$\left|1-\frac{u}{u_j}\right|^2 = \left|1-e^{i(\alpha-\alpha_j)}\right|^2 = \left\{1-e^{i(\alpha-\alpha_j)}\right\}\left\{1-e^{-i(\alpha-\alpha_j)}\right\} = 2-2\cos(\alpha-\alpha_j) = 4\sin^2\frac{1}{2}(\alpha-\alpha_j).$$

Donc $\quad \left|1-\dfrac{u}{u_j}\right| = 2\left|\sin\dfrac{1}{2}(\alpha-\alpha_j)\right|,$

qui donne, dans le voisinage de α_j : $(\alpha_j-\delta,\ \alpha_j+\delta)$,

$$\frac{2}{\pi}\left|\alpha-\alpha_j\right| \leqslant \left|1-\frac{u}{u_j}\right| \leqslant 2.$$

Done on a

$$\left(\int_{\alpha_j-\delta}^{\alpha_j}+\int_{\alpha_j}^{\alpha_j+\delta}\right)\log\left\{\frac{2}{\pi}|\alpha-\alpha_j|\right\}d\alpha \leqslant \left(\int_{\alpha_j-\delta}^{\alpha_j}+\int_{\alpha_j}^{\alpha_j+\delta}\right)\log\left|1-\frac{u}{u_j}\right|d\alpha \leqslant \int_{\alpha_j-\delta}^{\alpha_j+\delta}\log 2\,d\alpha,$$

c'est-à-dire

$$2\delta\log\left(\frac{2\delta}{\pi e}\right) \leqslant \left(\int_{\alpha_j-\delta}^{\alpha_j}+\int_{\alpha_j}^{\alpha_j+\delta}\right)\log\left|1-\frac{u}{u_j}\right|d\alpha \leqslant 2\delta\log 2,$$

on tire de la

$$\lim_{\delta\to+0}\left(\int_{\alpha_j-\delta}^{\alpha_j}+\int_{\alpha_j}^{\alpha_j+\delta}\right)\log\left|1-\frac{u}{u_j}\right|d\alpha=0.$$

Par conséquent, la valeur de l'intégrale

$$I\equiv\frac{1}{2\pi}\int_0^{2\pi}\log\left|1-\frac{u}{u_j}\right|d\alpha$$

$$=\lim_{\delta\to+0}\frac{1}{2\pi}\left\{\int_0^{\alpha_j-\delta}+\int_{\alpha_j-\delta}^{\alpha_j}+\int_{\alpha_j}^{\alpha_j+\delta}+\int_{\alpha_j+\delta}^{2\pi}\right\}\log\left|1-\frac{u}{u_j}\right|d\alpha$$

est finie. On a, d'une part,

$$I=\frac{1}{2\pi}\int_0^{2\pi}\log\left|2\sin\frac{1}{2}(\alpha-\alpha_j)\right|d\alpha$$

$$=\frac{1}{2\pi}\int_0^{2\pi}\log\left|2\sin\frac{1}{2}\alpha\right|d\alpha$$

$$=\frac{1}{2\pi}\int_0^{2\pi}\log\left(2\sin\frac{\alpha}{2}\right)d\alpha,$$

qui peut s'écrire sous la forme

$$(2.\ 5)\qquad I=\frac{1}{\pi}\int_0^{\pi}\log(2\sin\theta)d\theta,$$

où $\alpha=2\theta$. On a, d'autre part,

$$I=\frac{1}{\pi}\int_0^{\pi}\log\left(2\sin\frac{\alpha}{2}\right)d\alpha,$$

qui peut s'écrire, en posant α par $\pi-\alpha$,

$$=\frac{1}{\pi}\int_0^{\pi}\log\left(2\cos\frac{\alpha}{2}\right)d\alpha\,;$$

donc on a

$$(2.\ 6)\qquad 2I=\frac{1}{\pi}\int_0^{\pi}\log(2\sin\alpha)d\alpha.$$

Par (2. 5) et (2. 6), on a

$$2I=I,\qquad\text{donc } I=0.$$

En résumé, pour u_j (où $|u_j|=1$), on a

$$(2.\ 7)\qquad \frac{1}{2\pi}\int_0^{2\pi}\log|u-u_j|d\alpha=\frac{1}{2\pi}\int_0^{2\pi}\log\left|1-\frac{u}{u_j}\right|d\alpha$$

$$=0,\quad (j=p+1,\ p+2,\ldots,q).$$

Pour $u_j(j=q+1,\ q+2,\ldots,n)$ (où $|u_j|>1$), on a

$$\frac{1}{2\pi i}\int_{|u|=1}\frac{\log(u-u_j)}{u}du=\frac{1}{2\pi}\int_0^{2\pi}\log(u-u_j)\,d\alpha$$

$$=\log(-u_j),$$

donc on a

$$(2.\ 8)\qquad \frac{1}{2\pi}\int_0^{2\pi}\log|u-u_j|d\alpha=\log|u_j|,\quad (j=q+1,\ldots,n).$$

3. Par conséquent, en désignant par k le premier entier tel qu'on ait $|u_k| \neq 0$ (où $1 \leqslant k \leqslant p$), on a

$$\frac{1}{2\pi}\int_0^{2\pi} \log|\psi(u, v)|\, da = \log|u_{q+1}\dots u_n| = \log|u_k\dots u_n| - \log|u_k\dots u_q|, \quad (1 \leqslant k \leqslant p);$$

c'est-à-dire

$$\frac{1}{2\pi}\int_0^{2\pi} \log|\psi(u, v)|\, da > \log|u_k\dots u_n|, \quad (1 \leqslant k \leqslant p).$$

En supposant que tous $u_j \neq 0$, on a

$$\psi(0, v) = (-1)^n u_1 u_2\dots u_n,$$

et

$$\frac{\psi(0, v)}{(-1)^{k-1} u_1 u_2\dots u_{k-1}} = (-1)^{n-k-1} u_k\dots u_n,$$

parce que

$$\left.\frac{\psi(u, v)}{(u-u_1)(u-u_2)\dots(u-u_{k-1})}\right|_{u=0} = (-1)^{n-k-1} u_k\dots u_n.$$

Si $k=1$, on a

$$(3.\ 1) \qquad \frac{1}{2\pi}\int_0^{2\pi} \log|\psi(u, v)|\, da \geqslant \log|\psi(0, v)|,$$

et si $k>1$, on a

$$(3.\ 2) \qquad \frac{1}{2\pi}\int_0^{2\pi} \log|\psi(u, v)|\, da \geqslant \log|u_k\dots u_n| = \log\left|\frac{\psi(u, v)}{(u-u_1)(u-u_2)\dots(u-u_{k-1})}\right|_{u=0}.$$

Or la fonction $\psi(0, v)$ est holomorphe dans $|v| \leqslant 1$, et la fonction $\psi(0, re^{i\beta})$ peut avoir les zéros en nombre fini pour $r(<r+\varepsilon<1)$; et l'on a, pour une certaine valeur de r (ces valeurs $r_1, r_2, \dots, r_\nu, \dots$ peuvent être en nombre infini),

$$\psi(0, r_\nu e^{i\beta}) \neq 0 \qquad \text{(pour tout } \beta\text{)}.$$

Par conséquent, on a, sous la condition qu'il n'y ait pas de zéro sur $|v| = r_\nu$,

$$(3.\ 3) \qquad \frac{1}{2\pi}\int_0^{2\pi} \log|\psi(u, r_\nu e^{i\beta})|\, da \geqslant \log|\psi(0, r_\nu e^{i\beta})|.$$

On tire de la

$$(3.\ 4) \qquad \frac{1}{4\pi^2}\int_0^{2\pi} d\beta \int_0^{2\pi} \log|\psi(u, r_\nu e^{i\beta})|\, da \geqslant \frac{1}{2\pi}\int_0^{2\pi} \log|\psi(0, r_\nu e^{i\beta})|\, d\beta.$$

Donc en désignant par

$$\lambda_1, \lambda_2, \dots, \lambda_\mu \qquad (\mu : \text{fini})$$

les modules des zéros de $\psi(0, v)$ dans le cercle $|v|=r_\nu$, on a, par la formule de Jensen,

$$\frac{1}{4\pi^2}\int_0^{2\pi} d\beta \int_0^{2\pi} \log|\psi(e^{i\alpha}, r_\nu e^{i\beta})|\, d\alpha$$

$$(3.\ 5) \qquad \geqslant \log|\psi(0, 0)| + \log\frac{r_\nu^\mu}{\lambda_1 \lambda_2 \ldots \lambda_\mu}$$

$$\geqslant \log|\psi(0, 0)|.$$

Par conséquent, on a, pour $r=r_1, r_2, \ldots, r_\nu, \ldots \to 1-0$,

$$(3.\ 6) \qquad \frac{1}{4\pi^2}\int_0^{2\pi} d\beta \int_0^{2\pi} \log|\psi(e^{i\alpha}, re^{i\beta})|\, d\alpha \geqslant \log|\psi(0, 0)|.$$

4. Or la fonction $\psi(u, v)$ aura les nul-lignes dans le domaine ou sur sa frontière. Désignons par l l'ensemble de ces lignes dont la mesure plane est nulle, et désignons par $D(l)$ une partie du domaine A de (α, β), excluant l à l'extérieur et pouvant tendre vers A. Alors on voit que, pour une certaine valeur de $D(l)$, l'intégrale double

$$(4.\ 1) \qquad \iint_{D(l)} \log|\psi(u, v)|\, du d\beta$$

est finie, parce que la fonction $\log|\psi(u, v)|$ est continue dans le domaine $D(l)$. Au plus, pour $D(l)\to A$, l'intégrale double (4. 1) converge vers une valeur finie et déterminée, c'est-à-dire

$$(4.\ 2) \qquad \int_0^{2\pi}\int_0^{2\pi} \log|\psi(e^{i\alpha}, e^{i\beta})|\, du d\beta = \lim_{D(l)\to A} \iint_{D(l)} \log|\psi(u, v)|\, du d\beta.$$

Or on a

$$\iint_{D(l)} \log|\psi(u, v)|\, du d\beta = \int d\beta \int_{D(l)} \log|\psi(u, v)|\, d\alpha.$$

Donc on a à la limite $D(l)\to A$

$$(4.\ 3) \qquad \iint_A \log|\psi(u, v)|\, du d\beta = \int d\beta \int_A \log|\psi(u, v)|\, d\alpha.$$

En particulier on a

$$(4.\ 4) \qquad \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi} \log|\psi(e^{i\alpha}, re^{i\beta})|\, du d\beta = \frac{1}{4\pi^2}\int_0^{2\pi} d\beta \int_0^{2\pi} \log|\psi(e^{i\alpha}, re^{i\beta})| d\alpha.$$

Donc on a

$$\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi} \log|\psi(e^{i\alpha}, re^{i\beta})|\, du d\beta \geqslant \log|\psi(0, 0)|.$$

Tendant r vers un on a

$$(4.\ 5) \qquad \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi} \log|\psi(e^{i\alpha}, e^{i\beta}) du d\beta \geqslant \log|\psi(0, 0)|.$$

5. On a de même

$$(5.\ 1)\qquad \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\log|g(e^{i\alpha},\ e^{i\beta})|\,d\alpha d\beta=\frac{1}{4\pi^2}\int_0^{2\pi}d\beta\int_0^{2\pi}\log|g(e^{i\alpha},\ e^{i\beta})|\,d\alpha,$$

$$\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\log|e^{i\alpha}-u_0|\,d\alpha d\beta=\frac{1}{4\pi^2}\int_0^{2\pi}d\beta\int_0^{2\pi}\log|e^{i\alpha}-u_0|\,d\alpha$$

$$=0,$$

et

$$\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\log|e^{i\beta}-v_0|\,d\alpha d\beta=0;$$

et l'on a

$$\log|u_0|<0\quad\text{et}\quad\log|v_0|<0.$$

Par conséquent, on a, en vertu de (1. 4), l'inégalité suivante :

$$(5.\ 2)\qquad \log|g(0,\ 0)|<\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\log|g(e^{i\alpha},\ e^{i\beta})|\,d\alpha d\beta,$$

qui est l'inégalité voulue nécessaire dans notre théorie de la quasi-analyticité.

Je suis heureux de pouvoir exprimer mon profond remerciement au professeur M. Tosizô Matumoto, au Maître qui a bien voulu lire mon manuscrit et qui m'a fait quelques remarques très utiles.

Ein anderer Beweis des Hilfssatzes im Problem über Grundwasserströmung

von

Toshizô Matsumoto

(Eingegagen am 30 Mai, 1942)

Im Problem der stationären Potentialbewegung des Grundwassers, sei

$$W=\phi+i\psi=f(z)$$

das komplexe Potential, wo $z=x+iy$ ist. Wir nehmen den Fall an, wo die Wasserströmung sehr langsam ist. u, v seien die Komponenten der Geschwindigkeit, dann sind

$$u=\frac{\partial\phi}{\partial x}=\frac{\partial\psi}{\partial y},$$

$$v=\frac{\partial\phi}{\partial y}=-\frac{\partial\psi}{\partial x},$$

$$w=u-iv=\frac{dW}{dz}.$$

Das Grundwasser ist im Allgemeinen begrenzt durch einige durchlässige, oder undurchlässige Schichten, Sickerstrecken und freie Oberflächen. Es ist bekannt, dass sich die Randbedingen für jede Begrenzung des Wassers in der Form

$$\begin{cases} ax+by+c\phi+d\psi=e, \\ a'x+b'y+c'\phi+d'\psi=e' \end{cases}$$

schreiben lassen[1], wobei die Konstanten reell sind. So haben wir nach Davison-Rosenhead[2], für die Randbedingungen die Gleichungen

$$\begin{cases} \Im(mz+nW)=e, \\ \Im(m'z+n'W)=e' \end{cases} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

wo I den imaginären Teil bedeutet und die Konstanten m, n, m', n' im Allgemeinen komplex sind. Daher die Randkurve in der hodographen Ebene (u, v) befriedigt die Gleichung

1. Z, B., Hamel, Über Grundwasserströmung, Zeitschrift für angewandte Math. u. Mech. **14** (1934).

2. Davison-Rosenhead, Some cases of the steady two-dimensional percolation of water through ground, Proceed. Roy. Soc., London, **175** (1940).

$$\Im\left(\frac{m+nw}{m'+n'w}\right)=0. \quad \ldots\ldots\ldots\ldots(2)$$

Der wichtige Hilfssatz von Davison-Rosenhead lautet folgendermassen. *Die Kurve* (2) *lässt sich in der* Ω*-Ebene in eine Gerade transformieren, wo*

$$\Omega\equiv\lambda+i\mu=W-w_0 z$$

angenommen ist und w_0 *ein Punkt von* (2) *ist.*

In den folgenden Zeilen wollen wir einen Beweis, der von dem ihrigen verschieden ist. Wir setzen

$$w'=\frac{m+nw}{m'+n'w},$$

dann ist

$$w=\frac{m'w'-m}{-n'w'+n}.$$

Nach (2), haben wir

$$\Im w'=0,$$

welche eine Gerade in w'-Ebene darstellt. Daher ist die entsprechende Kurve in w-Ebene ein Kreis. Nun

$$d\Omega=d(\lambda+i\mu)=(w-w_0)dz.$$

Sei

$$w_0=\frac{m'w_0'-m}{-n'w_0'+n},$$

dann ist

$$\Im w_0'=0,$$

und

$$w-w_0=\frac{(m'n-mn')(w'-w_0')}{(-n'w'+n)(-n'w_0'+n)}.$$

Daher

$$\frac{d\Omega}{dz}=\frac{d}{dz}(\lambda+i\mu)$$

$$=\frac{m'n-mn'}{(-n'w'+n)(-n'w_0'+n)}(w'-w_0').$$

Zu Bemerken ist, dass $w'-w_0'$ reell ist. Nach (1) ist

$$\Im(m'z+n'W)=\text{konstant}.$$

Wenn man setzt

$$m'z+n'W=A+iB,$$

dann ist B konstant. Daher

$$m'+n'w=\frac{dA}{dz}$$

andererseits $$= \frac{m'n - mn'}{-n'w' + n}.$$

Zusammengefasst haben wir

$$\frac{d\lambda}{dz} + i\frac{d\mu}{dz} = \frac{dA}{dz}\frac{w' - w_0'}{-n'w_0' + n}.$$

Folglich ist

$$d\lambda + id\mu = dA \times (w' - w_0')\frac{1}{-n'w_0' + n}.$$

Die ersten zwei veränderlichen Faktoren sind reell. Daher ist $d\lambda : d\mu$ konstant, was zu beweisen war.

A Note on Fowler's Differential Equation, II

By

Toshizô Matsumoto

(Received August 11, 1942.)

1. For the unique existence and vanishing in finiteness of the solution satisfying the initial condition

$$\theta(+0)=C, \quad (0<C<\infty) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

(Emden's solution) of Fowler's differential equation

$$\frac{d}{d\xi}\left(\xi^{\lambda}\frac{d\theta}{d\xi}\right)+\xi^{\lambda}\theta^{n}=0, \quad (\lambda\geqslant 0,\ n\geqslant 0) \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

it is after Sansone necessary and sufficient that

$$2\lambda-n+1>0^{1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

holds. To prove this, Mr. Sansone has introduced the most important identity,

$$\frac{2\lambda-n+1}{2}\int_{0}^{\xi}\xi^{\lambda}\left(\frac{d\theta}{d\xi}\right)^{2}d\xi=\xi^{\lambda+1}\theta^{n+1}(\xi)+(\lambda+1)\xi^{\lambda}\theta(\xi)$$
$$+\frac{n+1}{2}\xi^{\lambda}\theta'^{2}(\xi). \quad \ldots\ldots(4)$$

In the previous note the present writer has given, probably the most natural method to arrive at this identity. In this note he intends chiefly to show briefly that quite the same method may be applied to the general Fowler's differential equation

$$\frac{d}{dx}\left(x^{\rho}\frac{dy}{dx}\right)+bx^{\sigma}y^{n}=0. \quad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

For simplicity we may suppose that the constants ρ, σ, n, b are positive. Then the required identity is (in the indefinite integral form)

$$\left[\sigma-\frac{n+1}{2}(\rho-1)+1\right]\int x^{\rho}\left(\frac{dy}{dx}\right)^{2}dx=bx^{\sigma+1}y^{n+1}$$
$$+(\sigma+1)x^{\rho}y\frac{dy}{dx}+\frac{n+1}{2}x^{\rho+1}\left(\frac{dy}{dx}\right)^{2}+C. \quad \ldots(6)$$

Here if we put $\rho=2$, $\sigma=\lambda$, we shall have (4).

2. The differential equation (5) is nothing but

1. For the literature, see the previous note. These Memoirs vol. 24, No. 2.

$$x\frac{d^2y}{dx^2}+\rho\frac{dy}{dx}+bx^{\sigma-\rho+1}y^n=0. \quad \cdots\cdots\cdots\cdots(7)$$

To get rid of the factor of y'', we have to put

$$x=e^{\rho u} \quad \text{or} \quad u=\frac{1}{\rho}\log x. \quad \cdots\cdots\cdots\cdots(8)$$

Then (7) becomes

$$\frac{d^2y}{du^2}+\rho(\rho-1)\frac{dy}{du}+b\rho^2e^{\rho(\sigma-\rho+2)u}y^n=0. \quad \cdots\cdots\cdots\cdots(9)$$

To chancell the term of y', we have to put

$$y=e^{-\binom{\rho}{2}u}v \quad \text{or} \quad v=ye^{\binom{\rho}{2}u}. \cdots\cdots\cdots\cdots(10)$$

Then (9) becomes

$$\left.\begin{aligned} &\frac{d^2v}{du^2}-\binom{\rho}{2}^2v+b\rho^2e^{pu}v^n=0, \\ \text{where}\quad &p\equiv\rho(\sigma-\rho+2)-(n-1)\binom{\rho}{2} \\ &=\rho\left[\sigma-\frac{n+1}{2}(\rho-1)+1\right]. \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots(11)$$

Remark that for $\rho=2$, $\sigma=\lambda$, we have $p=2\lambda-n+1$. As usual we write this equation as follows.

$$\frac{d}{du}\left[\frac{dv}{du}-\binom{\rho}{2}v\right]+\binom{\rho}{2}\left[\frac{dv}{du}-\binom{\rho}{2}v\right]=-b\rho^2e^{pu}v^n.$$

Multiplying by $2\left[\frac{dv}{du}-\binom{\rho}{2}v\right]$ and integrating, we shall have at last

$$\left[\frac{dv}{du}-\binom{\rho}{2}v\right]^2+2\binom{\rho}{2}\int\left[\frac{dv}{du}-\binom{\rho}{2}v\right]^2du$$
$$=-\frac{2b\rho^2}{n+1}e^{pu}v^{n+1}+2b\rho^2\left\{\frac{p}{n+1}+\binom{\rho}{2}\right\}\int e^{pu}v^{n+1}du+C,$$

under the assumption that $n+1\neq0$. By aid of (11), we have after easy calculations

$$2b\rho^2\int e^{pu}v^{n+1}du=-2\left[\frac{dv}{du}-\binom{\rho}{2}v\right]v+2\int\left[\frac{dv}{du}-\binom{\rho}{2}v\right]^2du.$$

So we have finally the identity,

$$p\int\left[\frac{dv}{du}-\binom{\rho}{2}v\right]^2du$$
$$=b\rho^2e^{pu}v^{n+1}+\left\{p+(n+1)\binom{\rho}{2}\right\}\left[\frac{dv}{du}-\binom{\rho}{2}v\right]v$$
$$+\frac{n+1}{2}\left[\frac{dv}{du}-\binom{\rho}{2}v\right]^2+C. \quad \cdots\cdots\cdots\cdots(12)$$

Returning to the original variables, we have the required identity (6).

3. We should observe whether our equation (5) may be transformed into an equation of the form (2). For this, by easy calculations, we have the result as follows.

If $\rho>1$, then by the substitution

$$x=t^k, \quad k=\frac{1}{\rho-1}>0,$$

(5) may be transformed into

$$\frac{d}{dt}\left(t^2\frac{dy}{dt}\right)+\frac{b}{(\rho-1)^2}t^{\frac{\sigma+1}{\rho-1}-1}y^n=0. \quad \cdots\cdots\cdots\cdots(13)$$

Further if $n\neq 1$, $b>0$, then by

$$Ay=\eta, \quad A=\sqrt[n-1]{\frac{b}{(\rho-1)^2}}>0,$$

(13) becomes

$$\frac{d}{dt}\left(t^2\frac{d\eta}{dt}\right)+t^{\frac{\sigma+1}{\rho-1}-1}\eta^n=0. \quad \cdots\cdots\cdots\cdots(14)$$

Here we have $\lambda=\dfrac{\sigma+1}{\rho-1}-1$. Hence the fundamental constant becomes

$$2\lambda-n+1=2\frac{\sigma-\dfrac{n+1}{2}(\rho-1)+1}{\rho-1}=\frac{p}{\binom{\rho}{2}}. \quad \cdots\cdots(15)$$

Thus we see that not all equations (5) may be transformed into (2), (preserving the coordinate origin). Moreover we notice that for $\lambda>0$, it is necessary that

$$\sigma-\rho+2>0. \quad \cdots\cdots\cdots\cdots(16)$$

4. Now we consider such solution

$$\left.\begin{aligned} &y(x)>0, \quad \text{for} \quad 0<x<x_0 \ (<\infty)\\ &y(+0)=C, \quad (0<C<\infty)\end{aligned}\right\} \quad \cdots\cdots\cdots\cdots(17)$$

If our integral satisfies the condition that

$$x^\rho y'\Big|_{x\to+0}=0 \quad \text{or} \quad x^{\frac{\rho+1}{2}}y'\Big|_{x\to+0}=0, \quad \cdots\cdots\cdots\cdots(18)$$

according as $\rho<1$ or $\rho\geqq 1$, then by (6) we have

$$\left[\sigma-\frac{n+1}{2}(\rho-1)+1\right]\int_0^x x^\rho\left(\frac{dy}{dx}\right)^2dx$$

$$=bx^{\sigma+1}y^{n+1}+(\sigma+1)x^\rho y\frac{dy}{dx}+\frac{n+1}{2}x^{\rho+1}\left(\frac{dy}{dx}\right)^2. \quad \cdots\cdots(19)$$

By (5), $x^\rho\dfrac{dy}{dx}$ decreases, a fortiori does so $\dfrac{dy}{dx}$. $(\rho\geqq 0)$ If $y(x_0)=0$,

then $\left(\frac{dy}{dx}\right)_{x=x_0}<0$. Hence by (18)

$$\left[\sigma-\frac{n+1}{2}(\rho-1)+1\right]\int_0^{x_0}x^\rho\left(\frac{dy}{dx}\right)^2dx=\frac{n+1}{2}x_0^{\rho+1}\left(\frac{dy}{dx}\right)_0^2>0.$$

So we have the necessary condition

$$\sigma-\frac{n+1}{2}(\rho-1)+1>0. \quad \text{.....(20)}$$

5. At first let us examine the first condition $\lim_{x\to+0}x^\rho y'(x)=0$. By (5) we have for $\varepsilon>0$

$$x^\rho y'(x)\Big|_\varepsilon^x=-b\int_\varepsilon^x x^\sigma y^n dx. \quad \text{.....(21)}$$

Therefore we have

$$\lim_{x\to+0}x^\rho y'(x)=a, \quad \text{.....(22)}$$

where a is finite determinate. If $a\neq0$, then supposing $a>0$, we may, for any number a', $(0<a'<a)$ find $\delta>0$, such that

$$0<a'<x^\rho y'(x)<a \quad \text{for} \quad 0<x<\delta.$$

Hence for $0<\varepsilon<x<\delta$, we have

$$\left.\begin{aligned}&\frac{a'}{1-\rho}\left(\frac{1}{x^{\rho-1}}-\frac{1}{\varepsilon^{\rho-1}}\right)<y(x)-y(\varepsilon)\\&\qquad<\frac{a}{1-\rho}\left(\frac{1}{x^{\rho-1}}-\frac{1}{\varepsilon^{\rho-1}}\right), \quad (\rho\neq1)\\ \text{or}\\&a'\log\frac{x}{\varepsilon}<y(x)-y(\varepsilon)<a\log\frac{x}{\varepsilon}, \quad (\rho=1)\end{aligned}\right\} \quad \text{.....(23)}$$

If $\rho\geqslant1$, we should have $y(+0)=-\infty$ which is contrary to the initial condition $y(+0)=C$. In case of $a<0$, the same contradiction occurs. Therefore it ought to be that

$$\lim_{x\to+0}x^\rho y'(x)=0, \quad (\rho>1) \quad \text{.....(24)}$$

Consequently by (21) we have

$$x^\rho y'(x)=-b\int_0^x x^\sigma y^n dx.$$

Now

$$\lim_{x\to+0}x^{\frac{\rho+1}{2}}y'(x)=-\lim_{x\to+0}\frac{b}{x^{\frac{\rho-1}{2}}}\int_0^x x^\sigma y^n dx$$

$$=-\frac{b}{\frac{\rho-1}{2}}\lim_{x\to+0}\frac{x^\sigma y^n}{x^{\frac{\rho-1}{2}-1}},$$

provided this last limit exists. It exists certainly. The limiting value is either zero or negative. If

$$x^{\frac{\rho+1}{2}}y'(x)<-A, \quad \text{for} \quad 0<x<\delta,$$

then
$$y(x)-y(\varepsilon)<-A\int_{\varepsilon}^{x}\frac{dx}{x^{\frac{\rho+1}{2}}}.$$

For $\varepsilon\to+0$, this inequality becomes absurd. Therefore we have

$$\lim_{x\to+0}x^{\frac{\rho+1}{2}}y'(x)=0, \quad (\rho>1) \qquad \text{.....(25)}$$

Thus one part of (18) has been verified and hence we may conclude that (19) is valid for $\rho\geqslant 1$, without assuming $x^{\frac{\rho+1}{2}}y'\Big|_{x\to+0}=0$.

In case of $\rho<1$, putting

$$\frac{x^{1-\rho}}{1-\rho}=u, \quad \text{or} \quad x=(1-\rho)^{\frac{1}{1-\rho}}u^{\frac{1}{1-\rho}}, \qquad \text{.....(26)}$$

(5) will be transformed into

$$\left.\begin{aligned} &x^{\rho}\frac{dy}{dx}=\frac{dy}{du},\\ &\frac{d^2y}{du^2}+Bu^{\frac{\sigma+\rho}{1-\rho}}y^n=0, \end{aligned}\right\} \qquad \text{.....(27)}$$

where $B\equiv b(1-\rho)^{\frac{\sigma+\rho}{1-\rho}}>0.$

For our solution $y(u)$, we have by (22)

$$\lim_{u\to+0}\frac{dy}{du}=a. \quad \text{(finite determinate)}$$

Judging from (23), a may not be zero. For if $n\geqslant 1$, then by the general existence theorem, (27) admits the unique integral with the initial conditions

$$y(0)=C, \quad y'(0)=a,$$

for any C and a. Therefore in the case of $\rho<1$, the identity (19) is only true on condition that $x^{\rho}y'\Big|_{x\to+0}=0$.

On the Possibility of Formation and Persistence of the Amorphous Layer on Polished Metal Surface and in Intercrystalline Boundaries

by

Usaburo Yoshida

(Received August, 11, 1942.)

Abstract

The possibility of formation of the amorphous layer on polished metal surfaces and in intercrystalline boundaries by plastic deformation of metals is infered. The liquid layer at high temperatures or the amorphous layer at low temperatures, when once formed in intercrystalline boundaries, is reasoned to be persistent irrespectively of the temperature change, by keeping the thickness of the layer in equilibrium with the temperature. Lastly it is stated that Mr. Hasiguti's objection to the writer's theory of recrystallization can not be accepted.

Introduction

Beilby's hypothesis assuming the formation of an amorphous layer on the surface of metals by polishing and in the intercrystalline boundaries of metals by plastic deformation is a subject variously discussed for a long time. This is a very important problem, and whether such an amorphous layer really exists or not is a key point to determine the direction of the general tendency of the theory of metals. In the previous papers[1] concerning the recrystallization and plastic deformation of metals, the explanation was made by assuming the presence of amorphous layer; and now the possibility of its formation and persistence will be considered in detail.

Formation of Amorphous Layer

F. P. Bowden and K. E. W. Ridler[2] measured thermo-electrically the temerature at the contact surface of two different metals by mutual sliding, and found that the temperature at the contact

1. U. Yoshida and K. Koyanagi: These Memoirs, **18**, 9, (1935); U. Yoshida, S. Nogata and Ch. Mitsuki: These Memoirs, **19**, 169, (1936); U. Yoshida: These Memoirs, **23**, 207, (1941); **23**, 351, (1941); X線, **2**, 152. (昭 16).

2. Proc. R. S., A, **154**, 640, (1936).

points could be raised up to the lower melting point of the two metals by sufficient magnitudes of the speed of sliding and of the compressive force. From this experiment F. P. Bowden and T. P. Hughes[1] reasoned the possibility of formation of the amorphous layer on the surface of metals by polishing and in the intercrystalline boundaries by plastic deformation. They considered that some microscopic localities on the polished surface of a metal or in the glide plane of the metal crystals are melted instantaneously by being heated locally by polishing or by plastic deformation. As the temperature of the bulk of the metal is not raised during this local melting, the molten localities solidify almost at the same instant as they are melted. Thus having no time to crystallize they solidify as amorphous solid by keeping unaltered the manner of molecular aggregation as in the liquid. Next F. P. Bowden and L. Leben[2] investigated the sliding motion of two metals minutely. They pressed by a spring a small polished metal ball against a polished flat surface of another metal, by constraining the metal ball in its lateral motion by bifilar springs. The flat metal was made to move very slowly by hydraulic pressure in the horizontal direction with a uniform velocity irrespectively of the frictional force against the ball; and the accompanying lateral motion of the ball was measured in a very magnified scale by means of reflection of a light beam from a mirror attached to the ball. The motion of the metal ball thus examined was found to be fluctuating very violently, and that it proceeds by the repetition of very small "stick and slip" process; the ball sticks to the plate at an instant and moves with it with the same velocity for a short time, then the ball slips against the plate suddenly and sticks again to the plate. In some cases using the combination of two metals of different kinds the temperature variation at the contact point was observed thermoelectrically by means of a string galvanometer, and it was found that the temperature rises violently only in the slipping period, but not at all in the sticking period. Bowden and Leben made their experiments with various conbinations of different metals and alloys having different hardness and melting points, and they examined microscopically the tracks of slide impressed on the surface of the flat plate during the sliding process. As to the ultimate mechanism of the stick and slip process, they could confirm by a careful measurement and

1. Proc. R. S., A., **160**, 575, (1937).
2. Proc. R. S., A, **169**, 371, (1939).

a microscopic examination that there was no direct corelation between the discontinuities of the sliding motion and the surface scratches, and came to the conclusion that the stick was caused by the creation of local metallic junctions formed by a sudden solidification of the molten localities on the contact surface, which were due to the local heating during the slipping process just previous to the sticking period.

All the experiments of Bowden and others indicate that by the frictional sliding of two solid surfaces, there takes place so unexpectedly a violent local heating that the local melting of the solids happens without much difficulty. As the local melting is entirely in microscopically narrow region, and the solids in bulk are not particularly heated in this case, the molten localities solidify suddenly as amorphous solids almost at the same time as they were melted. As regard to the formation of the amorphous solid by a rapid cooling of the melt, Luyet's experiment[1] seems to be worthy of mentioning. He pressed very suddenly a stream of running water at room temperature by two copper disks which had been cooled by liquid air. On examining very quickly the solidified piece of water through the crossed nicols, he found that the solidified water was amorphous, and the crystallization to ice was observed to occur only at much higher temperatures. In the case of common metals we are unable, of course, to detect the presence of their amorphous solid state conclusively. However, considering from Luyet's experiment, it seems not unreasonable to presume the formation of the amorphous solid by sufficiently rapid cooling in this case.

It was stated[2] in one of the previous papers that by the plastic deformation of metals a severe process, such as the destruction of the metal crystals into very fine crystallites having scattered orientation, occurred at the same time as the ideal crystal slip along the slip direction in the slip plane. If we consider the frictional sliding between neighbouring crystallites in the same way as in the case of the surface friction between metals, the formation of the amorphous solid layer between neighbouring crystallites will be readily accepted by imagining the occurrence of the local heating, melting and subsequent sudden solidification.

Bowden and others regard the local heating which takes place by the frictional sliding as the cause for the formation of the amorphous

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1. B. J. Luyet: Phys. R. **56**, 1244, (1939).
2. U. Yoshida: These Memoirs, **23**, 351, (1941); 應用物理, **11**. 1, (昭 17).

layer on the polished surface or in intercrystalline boundaries of metals. In addition to this cause, the writer reasonably assumes that the crystallites, which are smashed into very minute particles and severely distorted in their crystal lattices and endowed with internal stresses of considerable amount during the process of plastic deformation or of polishing, are much easier to melt and consequently their melting points fall noticeably. According to the writer's opinion[1] the phenomenon of recrystallization of cold worked metals proceeds by the growth of the crystal nuclei formed spontaneously in the melt at the crystal boundaries by consuming the old small and distorted crystallites. If the writer's opinion is to be admitted the above assumption that the smaller and more distorted crystals are easier to melt than larger and less distorted ones is necessary in explaining the mechanism of recrystallization. As the crystal lattice is most stable when there is no internal stress or lattice distortion, the potential energy of the constituent molecules of the crystal lattice is higher when it is internally stressed or distorted, and consequently the latent heat of fusion becomes smaller in this case. If we plot in graph the relation between the molecular latent heats of fusion of monoatomic elements and their melting points expressed in the absolute scale we can see clearly the general tendency that the melting point is lower when the molecular latent heat of fusion is smaller. Moreover, with the elements belonging to the face-centred cubic lattice and the close packed hexagonal lattice, where the manner of molecular arrangement is almost the same in both lattice types, the melting points are approximately proportional to the molecular latent heats of fusion. Considering from this view point it will not be unreasonable to imagine that the melting point of an element becomes lower than the normal value when its crystal lattice is distorted or stressed internally. Next, if we consider the case of extremely small crystallites similarly as in the case of very small liquid droplets, their vapour pressure ought to be much higher than the normal value; and consequently the latent heat of sublimation and the latent heat of fusion should be much reduced in this case. The lowering of the melting point in this case which just corresponds to the lowering of the boiling point of very small liquid droplets can be imagined by such decrease of the latent heat of fusion. Considering in the above way, the lowering of the

1. U. Yoshida: These Memoirs, **23**, 325, (1941).

melting point of the crystallites, when they are extremely minute and distorted in their lattice and internally stressed, can be clearly understood. According to the experiments made by Farren and Taylor,[1] when a metal or alloy is cold-worked the most part of the work done during this process is generated as heat, but the remaining part amounting to 5—15% is imparted in increasing the potential energy of the constituent molecules. This increase of the molecular potential energy corresponds at least mostly to the decrease of the latent heat of fusion of the crystallites, which are smashed into very minute ones and distorted in their lattice by the process of cold-working.

Very recently Jaeger and Zuitoff[2] measured at temperatures higher than about 500°C the specific heats of two specimens of cobalt, one composed of comparatively large crystals and the other of very fine crystallites deposited by electrolysis. They found that the latter had a smaller specific heat, and moreover that the specific heat of the latter increased and became equal to that of the former when its crystals had grown to a considerable size by recrystallization. Similar observations on cold worked metals and alloys were made by Sato,[3] Quinney and Taylor.[4] According to these authors some amount of energy is imparted as latent energy to the metals and alloys by the process of cold working, and this latent energy is reemitted on heating the metals and alloys at high temperatures. These facts are in accordance with the writer's view that the latent heat of fusion is smaller with smaller and distorted crystal, and consequently that the smaller and the distorted crystals are easier to melt than larger and the undistorted ones. When the specific heat of the specimen composed of very fine and distorted crystallites is measured at high temperatures, the distortion will be released and small crystallites will melt and gradually recrystallize into larger ones; and by this process of annealing and recrystallization, heat evolution of some amount takes place by virtue of the release of the distortion and of the preponderant latent heat of fusion of larger crystals as compared with that of smaller ones which melt and transform into larger ones by the recrystallization. Consequently the specific heat of the specimen will be reduced by this amount of heat evolved by the annealing and recrystallization.

1. W. S. Farren and G. I. Taylor: Proc. R. S., A, **107**, 422, (1925).
2. F. M. Jaeger and A. J. Zuitoff: Proc. Amsterdam, **43**, 815, (1940)
3. S. Sato: Sci. Rep. Tohoku Imp. Univ. **20**, 140, (1931).
4. H. Quinney and G. I. Taylor: Proc. R. S. **163**, 157, (1937).

If we consider in the above way, by the formation of the amorphous layer on a metal surface by polishing and in intercrystalline boundaries of a metal by plastic deformation, the temperature reached by the local heating does not need to be so high as the normal melting point of the metal, but is sufficient if it becomes the same with, or higher than, the decreased melting point of very small and distorted crystallites. The amorphous layer formed in intercrystalline boundaries softens in its softening temperature range, and becomes liquid when the temperature is raised still higher. In this state the crystal growth can be imagined to take place toward the liquid layer, and the question whether the liquid layer will be exhausted or not by such crystal growth becomes very important. However, for the writer's theory of recrystallization to be consistent, which assumes that the crystal growth by recrystallization takes place by means of an intermediary action of the liquid layer between neighbouring crystals, the liquid or amorphous layer should be permanent and persistent, and this point will be considered in the following.

Persistence of the Liquid or Amorphous Layer between Neighbouring Crystals

Let us suppose that two crystals of a substance are separated by a thin liquid layer of the same substance and that the crystals grow toward the intermediate liquid layer. As with most substances the volume contracts by crystallization, when thus crystals grow toward the intermediate liquid layer, the latter becomes subjected to a negative pressure. This negative pressure is enormous when the liquid layer is extremely thin. Let us consider, for example, that a thin layer of liquid water is sustained by its surface tension between two parallel plates. If we take the surface tension of water approximately as 70 dynes/cm, then the magnitude of the negative pressure becomes about one atmosphere with the width of 1/1000 mm of the layer of water. With several metals their surface tensions at temperatures above the melting points were measured and have been found to take the values of 3—25 times the value of water. If we take these values roughly as 10 times that of water, then the magnitude of the negative pressure of the melt existing between two neighbouring metal crystals will be 10 atmospheres with the thickness of 1/1000 mm of the layer of the melt. Moreover as the surface tension of a liquid increases with decreasing temperature, its value of the melt below the

melting point, which is the point in question in the present case, will be enormously greater than that above the melting point. If we take this roughly as 10 times that above the meltiug point, then the negative pressure of the melt of metals below the melting points will amount to about 100 atmospheres with 1/1000 mm thickness of the melt. Further, as the negative pressure increases in inverse proportion with the thickness of the melt, its amount will increase infinitely even to more than 1000 atmospheres when the layer of the melt becomes thinner than about 1/1000 mm and the temperature is still farther decreased.

When a liquid is subjected to a gegative pressure, its vapour pressure decreases from its normal value. This just corresponds to the case of a solution, where the vapour pressure and consequently the freezing point of the solvent decreases by virtue of the presence of the osmotic pressure; and the lowering of the freezing point of the melt subjected to a negative pressure in very narrow interstices between two neighbouring crystals can thus be understood from the lowering of its vapour pressure. When the temperature decreases more and the layer of the melt between the two neighbouring crystals becomes much thinner by the growth of the crystals the increase of the negative pressure and consequently the lowering of the freezing point will proceed endlessly until the last stage is reached, where the extremely thin liquid layer solidifies as an amorphous solid and the crystal growth is entirely suspended. The liquid layers having enormous negative pressures as was considered above will not always be present over all the crystal boundaries and magnitude of the negative pressures will not necessarily be uniform for all parts of the liquid layers, so that they can act as a uniform hydrostatic tension on all the surfaces of the crystals, but the negative pressures will differ from place to place and further there will remain some portions in the crystal boundaries where they are not wetted by the liquid layer in the case of crystallization in the melt and of the recrystallization of cold worked metals, so that the negative pressures exercise heterogeneous stresses to the crystals. This also assists in lowering the melting point of the metals by giving lattice distortions and internal stresses to the crystals.

As to the freezing of water and some other liquids kept in very narrow cavities and interstices of silica-gels, clays composed of very fine particles and similar substances, researches by the dilato-

metric[1] and calorimetric[2] methods have been made by many authors. According to these investigations the water and other liquids confined in very narrow cavities and interstices freeze only at the temperatures much lower than their normal freezing points. For example Bouyoucos and his co-workers have found that there still remains some liquid water without freezing in very narrow interstices of clay particles at as low a temperature as $-78°C$. The circumstances in this case are somewhat different from our case, where the liquid layer is the same substance as the crystals confining the liquid; but the essential cause for such remarkable lowering of the melting point seems to be the presence of an enormous negative pressure in the liquid layer, and consequently the above experiments may be looked upon as a confirmation of the writer's view.

The freezing point of the liquid layer confined between two neighbouring crystals decreases with the decrease of the thickness of the liquid layer, and there exists an equilibrium between the temperature and the thickness of the liquid layer. Thus when temperature falls by a certain degree from that corresponding to an equilibrium condition the crystals grow and the liquid layer becomes thinner and attains the new equilibrium value corresponding to the decreased temperature. In this way, when temperature is decreased continuously the liquid layer gets thinner and thinner until the last stage is reached, where the extremely thin liquid layer solidifies in an amorphous solid state and the crystal growth stops. In other words the layer of liquid or of amorphous solid, when once formed in the boundary space between two neighbouring crystals of the same substance in the case of crystallization form the melt or of recrystallization of polycrystalline metals, can persist as such for ever at all temperatures by adaptation to the temperature change with the variation of its width. When the temperature is raised in a substance in which the intercrystalline boundaries are cemented by the amorphous solid layer at room temperature, and when it attains the softening temperature of the amorphous layer, this layer turns to a liquid. As the

1. G. T. Bouyoucos and his co-workers: Mich. Agr. Coll. Expt. Sta. Tech. Bull., **24**, (1915); **27**, (1916); **31**, (1916); **36**, (1917); **37**, (1917); **42**, (1918); J. Agr. Res., **8**, (1917); **15**, (1918); **20**, (1920); **20**, (1921); Soils Sci., **11**, (1921).
H. W. Foote and Blair Saxton: J. Amer. Chem. Soc., **38**, 588, (1916); **39**, 627, 1103, (1917).
F. W. Parker: J. Amer. Chem. Soc., **43**, 1011, (1921).
Jones and Gortner: J. Phys. Chem., **36**, 387, (1932).
2. W. A. Patrick and W. A. Kemper: J. Phys. Chem., **42**, 369, (1938).

crystal nuclei can be formed in the liquid layer in this case, this softening temperature of the amorphous layer will be the lowest recrystallization temperature of the substance. When the temperature is further raised the thickness of the liquid layer increases correspondingly and it will attain a considerabie amount at the temperatures just below the melting point, as is revealed by the occurrence of the grooves of noticeable width at the crystal boundaries on the surface of the specimen.

On Mr. Hasiguti's Objection to the Writer's Theory of Recrystallization

Recently Hasiguti[1] considered the recrystallization process of cold-worked metals as a kind of "exchange of place" (Platzwechsel) of molecules as in the case of diffusion of metals, and applied the equation of velocity of chemical reaction of Boltzmann's type to the temperature variation of the velocity of recrystallization of copper and aluminium. For the activation energy thus calculated for the exchange of place of molecules he obtained the values of about ten times those of the heats of fusion of the respective elements, and concluded that the presence of such large values of the activation energy is a strong argument against the writer's theory of recrystallization which assumes the melting at the intercrystalline boundaries as an essential factor for the process. The literature cited by Hasiguti is only the first paper published on this subject by the writer and Koyanagi, and it seems that Hasiguti was then ignorant of the later papers and consequently the writer's opinion was not well understood by him. According to the writer's experience the crystal growth by recrystallization depends upon the relative contrast in the stability of the crystal lattice between the neighbouring crystals, and does not occur in one step, but goes on gradually in many steps by successively repeating the process of mutual eating between neighbouring crystals until the final state is reached, in which the growing powers of all the crystals are almost balanced. The crystal growth by recrystallization goes on in general very rapidly at first, but becomes slower gradually with the progress of the steps of recrystallization and finally it becomes almost stopped when an equilibrium of the growing power of crystals is nearly attained. Consequently the recrystallization velocity can not be taken

1. Proc. Phys. Math. Soc. Japan, **24**, 270, (1942); 日本金屬學會誌, **6**, 282 (昭 17).

as constant throughout the whole process as Hasiguti did. Moreover the equation of velocity of chemical reaction can be applied to the case where the microscopic change of the ultimate particles takes place only in one direction. For example, consider the case of the vaporization of liquid molecules from the surface of a liquid. If all the evaporating vapour molecules could be perfectly pumped away and no vapour molecules would come back to the liquid, then the equation under consideration could be applied for the velocity of evaporation. However, when there are some vapour molecules which come back to the liquid, then the microscopic changes of molecules are in two opposite directions: i. e. evaporation and condensation; and the macroscopic velocity of evaporation becomes the difference of two velocities of these two microscopic changes in opposite directions. Thus in our case. which may be called a "semi-equilibrium change," the equation under consideration can not be applied. The fact that Richardson's formula for the thermionic emission from a hot body can only be applied to the case when all the emitted electrons are perfectly taken away to the anode, so that the current saturates, is a good example for the unidirectional microscopic change. According to the writer's theory of recrystallization the crystal growth of either one of the two neighbouring crystals A and B takes place by its consuming the other by means of the intermediary action of the liquid layer existing between them. The microscopic changes of molecules in this case consist of four different kinds: dissolution of the molecules belonging to the crystal A into the liquid phase, the condensations of the liquid molecules to the surfaces of the crystals A and B, and the dissolution of the molecules belonging to B into the liquid phase; and the macroscopic velocity of the crystal growth in this case becomes the algebraic sum of the velocities of these four different microscopic changes. In other words, the crystal growth in our case proceeds by a duplicated semi-equilibrium change and the equation of velocity of chemical reaction as was used by Hasiguti is not applicable here.

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The Tensile Strength of Rubber and Rubber Molecule

By

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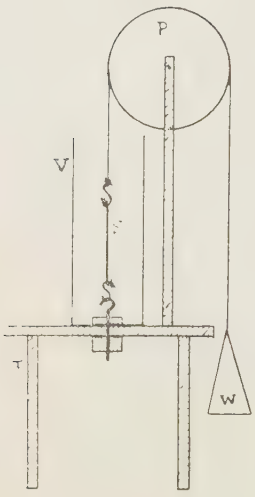
Abstract

The tensile strengths of crystallized crude rubber and vulcanized rubber are remarkably different from each other at room temperature, but are found to be almost the same at the temperature of liquid air. By assuming that the tensile strength of the crystallized rubber at this low temperature is entirely due to that of its chain molecules the force needed to break a chain molecule of rubber at its weakest point is estimated.

The writers prepared ribbons of smoked sheet rubber and vulcanized rubber, each of which was 0.5 cm wide, 0.3 cm thick and 6 cm long. After marking two points 1 cm apart on the surface of a ribbon, it was stretched quickly at room temperature by applying a load of about 700 % stretching degree in the case of smoked sheet rubber and of about 400 % stretching degree in the case of vulcanized rubber. Under these sufficient degrees of stretching the samples are presumed to be considerably crystallized and to be mostly relieved of intermolecular slipping by stretching. The stretched specimen was then broken at various temperatures by increasing the load, and its tensile strength was obtained from the value of the breaking load and the cross-sectional area at the instant of the break. The latter was calculated from the values of the cross-sectional area before stretching and the changes of length and density which were caused in stretching up to the final break. The actual experiment was carried on by using the apparatus as shown in Fig. 1. In this figure V is a vessel fixed firmly to the heavy table T, and S is the test piece of rubber which is to be stretched and broken by applying a load W over the pulley P. The tensile test was made at various temperatures ranging from 78°C to the liquid air temperature. After the specimen was stretched sufficiently at room temperature, it was heated or cooled by pouring a proper liquid or a liquid mixture kept at desired temperatures. Water was used for the temperatures higher than about

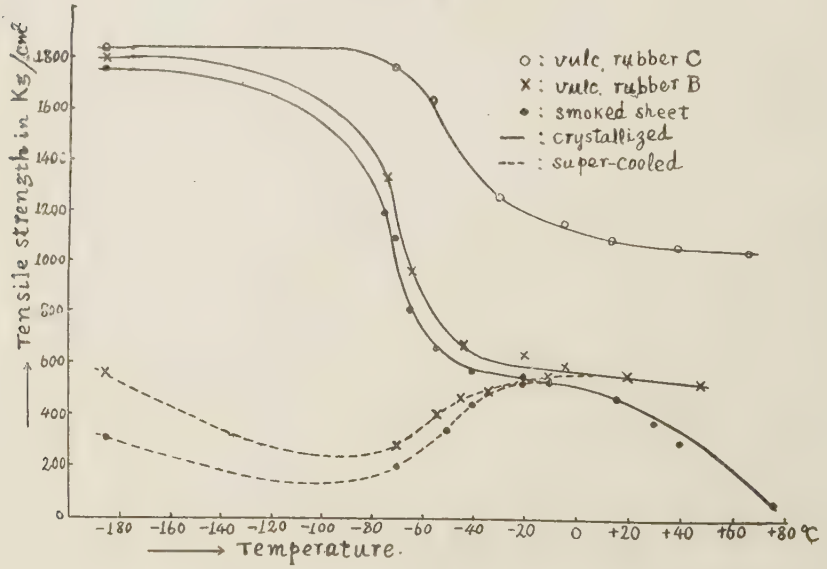
Fig. 1



10°C, and the liquid air at −185°C; and for intermediate temperatures acetone or alcohol mixed with dry ice were employed. Two different kinds of the vulcanized rubber were tested: viz. that of accelerator mixture and that of carbon mixture.

As a control the smoked sheet rubber and the vulcanized rubber were broken suddenly in the same manner as above by heating and cooling at various temperatures without any previous stretching. As stated in the previous papers,[1] when unstretched rubber is cooled suddenly at low temperatures it undergoes almost no crystallization and is hardened as an amorphous solid in super-cooled state. Consequently, by virtue of the predomi-

Fig. 2



nant intermolecular slipping, a considerable low value of the tensile strength is expected in this case when compared with the specimen cooled in stretched state. The results obtained by the present experiment are shown in Fig. 2, by taking the temperature as abscissa

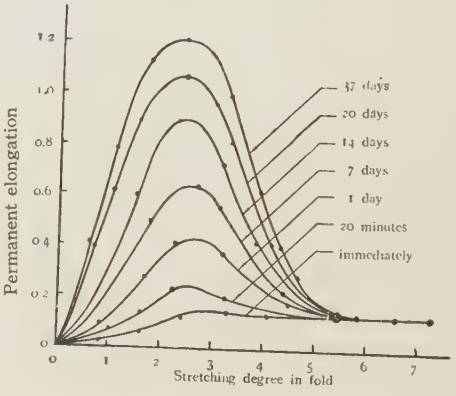
1. Ch. Park: These Memoirs, **22**, 259 (1939), **23**, 137 (1940).

and the tensile strength as ordinate. In this figure the curves drawn in full line refer to the specimens broken by being cooled or heated in sufficiently stretched state, those drawn in broken line refer to the specimens broken by being cooled or heated suddenly in unstretched state; and the dots, crosses and small circles represent respectively the tensile strengths of smoked sheet rubber, vulcanized rubber of accelerator mixture B and the vulcanized rubber of carbon mixture C. As is seen in the figure the tensile strengths of the smoked sheet rubber and the vulcanized rubber which are cooled or heated in sufficiently stretched state increase generally with decrease of the temperature. They are generally very different from each other, being considerably higher with the vulcanized rubber C, but they converge to almost the same value at the liquid air temperature. This point is especially noteworthy as will be described later. As to the smoked sheet rubber and the vulcanized rubber B, which are broken by being cooled suddenly in unstretched state, their tensile strengths behave entirely differently from the specimens kept stretched at low temperatures. As is expected, the tensile strengths decrease in this case, in contrast to the stretched specimens, with decrease of the temperature from about -20°C to about -70°C, and then increase slightly at the temperature of liquid air.

As to the ultimate mechanism of the breaking of the rubber ribbon by stretching two phenomena are conceivable: the mutual slipping between neighbouring chain molecules and the tearing of the chain molecules themselves at the weakest localities in their chain structure. When a ribbon of smoked sheet rubber is stretched very slowly at room temperature, it becomes gradually thinner at some portion without being crystallized noticeably and then undergoes the final rupture. As the elongation of the broken pieces is not much recovered on heating, the rupture of the rubber ribbon in this case seems to be mainly caused by the intermolecular slipping. However, in the present experiment, the rubber ribbons were broken by suddenly increasing the stretching load by being cooled in a strongly stretched or entirely unstretched state, and the rupture took place with a right section as if the ribbon was cut with a sharp knife, without becoming gradually thinner as is stated above. Thus by the rupture in this case, the tearing of the long chain molecules is presumable to have happened together with the inter-molecular slipping, though the proportion of these two factors will be different according to the conditions to which the test pieces are subjected.

Whether or not the rupture of the rubber ribbon in a certain case is mostly due to the tearing of the long chain molecules will be judged by knowing under what condition the inter-molecular slipping is hard to take place. Fig. 3, which has been once shown in a previous paper,[1] represents the permanent elongation of the smoked sheet rubber ribbons caused by the intermolecular slipping when the ribbons are kept stretched for different durations of time at room temperature. As is seen from the figure, the inter-molecular slipping decreases generally as the degree of crystallization increases by sufficient stretching; and with extreme stretching to greater than about 5.5 times the original length, no trace of the inter-molecular slipping can be detected even with the specimen kept for 37 days in the stretched state at room temperature, except a small permanent elongation caused by the process of the initial sudden stretching. On the contrary, when the crystallization is not predominant under insufficient stretching a noticeable inter-molecular slipping, which is roughly proportional to the stretching stress and the amount of uncrystallized part, proceeds gradually during the time the specimen is kept stretched. Further it is reported in the previous paper that the inter-molecular slipping is remarkable at high temperatures and decreases with decrease of the temperature. Consequently it may be infered from these facts that when an extremely stretched rubber ribbon is cooled to the temperature of dry ice or of liquid air the inter-molecular slipping becomes very difficult, and the tearing of the long chain molecules of rubber at the localities of the weakest interatomic cohesion becomes the main cause for the rupture by stretching of the specimen.

Fig. 3



The measurements of the permanent elongations of the vulcanized rubber ribbons of carbon mixture caused by the inter-molecular slipping in a stretched state were made. The rubber ribbons were kept stretched for various durations in three different temperature ranges of 12°—18°C, 30°—40°C and 50°—60°C. The permanent elongations of

1. Ch. Park: These Memoirs, **23**, 137 (1940).

the specimens were obtained as before by putting them in boiling water for a short time after releasing of the stretching tension so that they could completely contract, and then by measuring the amounts of elongation per original unit length. The results of measurement are shown in Figs. 4a, 4b and 4c. If we compare these figures with Fig.

Fig. 4a

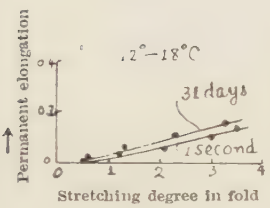


Fig. 4b

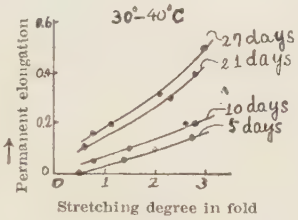
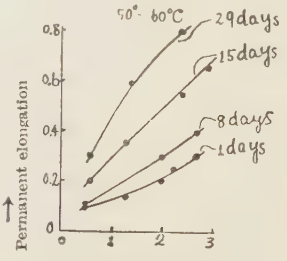


Fig. 4c



3, we find that the permanent elongation due to the inter-molecular slipping is very much smaller with vulcanized rubber than with unvulcanized smoked sheet. Though permanent elongation is considerable at high temperatures of 30°–40°C or 50°–60°C, it is almost unnoticeable at room temperature (12°–18°C) even with the stretching duration of 31 days; and there is hardly any difference detectable between the stretching of 31 days and that of only a second. This is one of the valuable properties of vulcanized rubber, and it seems to be caused by the hindrance of inter-molecular slipping by virtue of the strong side linkage between neighbouring chain molecules of the rubber, due to the presence of the sulphur molecules.

When unstretched rubber is cooled suddenly to such a low temperature as -30°C, the crystallization is suspended and it hardens as amorphous solid by being super-cooled as stated above. It is also stated previously, that the tensile strengths of the smoked sheet rubber and the vulcanized rubber which are cooled suddenly in unstretched state are remarkably low when compared with that cooled in sufficiently stretched state. This is evidently related to the super-cooling. The super-cooling becomes conspicuous and consequently the degree of crystallization gets unnoticeable with decrease of the cooling temperature. In the super-cooled state the intermolecular slipping is much easier to take place by virtue of the lack of some kind of the hooking effect between neighbouring molecules which is remarkable in the crystallized state. The fact that the tensile strength of the rubber ribbons

which are cooled suddenly in unstretched state decreases from -20°C to about -70°C is thus clearly understood by the increase of the degree of the super-cooling with decrease of the temperature. When the cooling temperature is still lowered to that of liquid air the tensile strenth increases slightly. By the sudden cooling to this low temperature the supercooling will be almost perfect, and a slight increase of the tensile strength at this temperature seems to be caused by the increased difficulty of the inter-molecular slipping due to the increased side cohesive force between neighbouring chain molecules.

The tensile strengths of the vulcanized rubber and smoked sheet rubber which are kept cooled in fully stretched state increase with decrease of the cooling temperature, that of the vulcanized rubber C being generally much higher than those of the other kinds. This superior tensile strength of the vulcanized rubber C can be explained by the interfering action of sulphur molecules upon inter-molecular slipping by virtue of the enhanced side linkage between neighbouring chain molecules; and the increase of the tensile strengths of the vulcanized rubber and the smoked sheet rubber with decrease of temperature can be ascribed to the increased difficulty of the inter-molecular slipping due to the increased degree of crystallization and of intermolecular side cohesion at low temperatures. The tensile strengths of the vulcanized rubber C and other kinds, which are considerably different at higher temperatures, converge almost to the same value at the temperature of liquid air. This point is especially noteworthy, and it seems to indicate that the tensile strengths of all the vulcanized and the smoked sheet rubbers at this low temperature are mainly related to the force which is necessary to tear the chain molecules of rubber; for, if they were due still considerably to the inter-molecular slipping, the remarkable differences among their values present at higher temperatures should also be present at the temperature of liquid air. Further, as is seen in Fig. 2, the tensile strength of the vulcanized rubber C attains at the temperature of dry ice almost to its maximum value assumed at the temperature of liquid air. This seems to indicate that the force necessary to tear a chain molecule of rubber is not much affected by the temperature.

Under the considerations made in the above way, the force necessary to tear the chain molecule of rubber was calculated by regarding the tensile strength of rubber at the temperature of liquid air as exclusively due to this force. It is known that when rubber is crys-

tallized by stretching the chain molecules of it are arranged parallel to the stretching direction, and that 4 such chain molecules pass through its unit crystal having the cross-sectional area of $8.54 \times 12.65 = 108$ A^2 in the direction perpendicular to the stretching direction. Thus if we assume that all rubber molecules in a rubber ribbon which is fully stretched and cooled to the temperature of liquid air are approximately fitted in the crystal lattice, the total number of chain molecules penetrating the cross-sectional area of 1 cm^2 will be $(4/1.08) \times 10^{14} = 3.7 \times 10^{14}$. Moreover if we take the tensile strength of the fully stretched rubber ribbon at the temperature of liquid air as 1850 Kg/cm^2, the force necessary to tear a chain rubber molecule becomes $(1.85 \times 10^6)/(3.7 \times 10^{14}) = 5 \times 10^{-9}$ g, which may be called "the tensile strength of the chain rubber molecule."

It is known that the decomposition of rubber into isoprene (C_5H_8), dipentene ($C_{10}H_{16}$) and heveene (constitution unknown) begins at the temperature of about 200°C; and this fact makes it possible to make a rough estimate of the energy necessary to decompose one isoprene group. The manner of thermal motion of each part of the long chain molecule is not of course obvious, but if the mean kinetic energy of an isoprene group is taken as the same with that of a gas molecule at the same temperature, then the simple kinetic theory of gases can be applied to this case. If we represent by m and $\bar{V}^2$ the mass and the mean square velocity of a gas molecule, then the average kinetic energy of a molecule at an absolute temperature T is given by

$$\frac{1}{2} m \bar{V}^2 = \frac{3}{2} \frac{R}{N} T,$$

where R is the gas constant ($R = 1.985$ cal/degree) and N is the Loschmidt number ($N = 6 \times 10^{23}$). If we take T as $200° + 273°$K, at which the decomposition of the rubber molecules into isoprene and others takes place, we get the value of

$$\frac{1}{2} m \bar{V}^2 = 9.8 \times 10^{-14} \text{ erg}$$

as the mean kinetic energy of a gas molecule. If this value is taken to be the same with the mean kinetic energy of an isoprene group as a whole at the same temperature, then this can be considered roughly to be the energy required to decompose one isoprene group from the rubber molecule, i. e. the energy needed to tear the chain rubber molecule at the locality of the weakest interatomic cohesion.

The tension acting between the two linking carbon atoms in a

chain rubber molecule at the locality of the weakest interatomic cohesion will differ according to their distance; and the value of the tensile strength of a chain rubber molecule obtained by the present experiment, can be looked upon as the maximum tension which the two linking carbon atoms can sustain. Thus if we consider that the energy needed to disjoin such carbon linkage is roughly equal to the work done in separating the two linking carbon atoms with the maximum tension for the distance of the order of atomic size, we get for this energy

$$5\times 10^{-9}\times 980\times(1\sim 2)\times 10^{-8}\fallingdotseq 5\times 10^{-14}\sim 10\times 10^{-14}\ \text{erg}$$

which is in good accord with the former estimation.

The above way of estimation of the energy required in breaking the weakest carbon linkage in the chain rubber molecule is very rough of course. However, the agreement between the values estimated in two different ways is satisfactory; and it may be looked upon as confirming the value obtained by the present experiment as of the right order for the tensile strength of the chain rubber molecule. The tensile strength of the chain rubber molecule is related to the locality of the weakest interatomic cohesion in it; and it will be natural to designate the part linked by a single bond between carbon atoms as such a weakest interatomic cohesion.

A Thermodynamical Research on the Phenomena of Melting and Crystallization

By

Usaburo Yoshida

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Abstract

As a continuation of the former papers the equilibrium between the free liquid molecules and the crystal nuclei, each composed of an immense number of the molecules, was investigated with various substances by applying van't Hoff's reaction isochore; and it was found that the melting point is well designated at the last stage of the nuclei decomposition, and that the relation between the melting point, the latent heat of fusion and its change with temperature was in good accord with the theory for various elements and compounds.

Introduction

In the former papers[1] the equilibrium between the free liquid molecules and the crystal nuclei, each composed of an infinite number of the molecules, was studied with monoatomic elements by applying van't Hoff's reaction isochore. In that case the change of the latent heat of fusion with temperature, which is mainly due to the difference of the specific heats of the melt and the crystal at the melting point, was neglected approximately; and the latent heat of fusion was taken to be constant and independent from the temperature for monoatomic elements. However, this is not correct in strict sense, the specific heats of the melt and the crystal are different in general at the melting point, slightly with monoatomic elements and remarkably with most of the chemical compounds. In the following such difference of two specific heats was taken into consideration, and its bearing on the ratio between the latent heat of fusion and the melting temperature was examined for various elements and compounds, which are provided with necessary data, by the aid of van't Hoff's reaction isochore.

1. U. Yoshida: These Memoirs, **24**, 1, 37 (1942).

Van't Hoff's Reaction Isochore for the Equilibrium between the Crystal Nuclei and the Free Liquid Molecules of a Substance

Let the number of the free molecules and of the crystal nuclei among the total number N of the molecules in a super-cooled liquid state of a substance be N_f and n_c respectively. If we represent by ν the number of the constituent molecules of a crystal nucleus, we have

$$N=N_f+\nu n_c \quad \cdots\cdots(1)$$

Let us define the ratio x of the number of free molecules and the number N_d of the total discrete particles which is the sum of N_f and n_c as the degree of decomposition of the crystal nuclei. Then we get

$$x=\frac{N_f}{N_d}=\frac{N_f}{N_f+n_c}, \quad \cdots\cdots(2)$$

$$1-x=\frac{n_c}{N_d}=\frac{n_c}{N_f+n_c}, \quad \cdots\cdots(3)$$

and the reaction constant K_c becomes

$$K_c=\frac{\left(\frac{N_f}{N_f+n_c}\right)^{\nu}}{\frac{n_c}{N_f+n_c}}=\frac{x^{\nu}}{1-x}. \quad \cdots\cdots(4)$$

If we represent by T the absolute temperature, by R the gas constant refering to one gram mol and by L the latent heat of fusion of the crystal nucleus per one gram mol; then the reaction isochore takes the form

$$\frac{d\log K_c}{dT}=\left(\frac{\nu}{x}+\frac{1}{1-x}\right)\frac{dx}{dT}=\frac{\nu L}{RT^2} \quad \cdots\cdots(5)$$

for a constant value of ν. By rewriting this equation we get

$$\frac{dx}{dT}=y\frac{L}{RT^2}, \quad \cdots\cdots(6)$$

where y represents

$$y=\frac{\nu x(1-x)}{\nu(1-x)+x}. \quad \cdots\cdots(7)$$

Next by differentiating (6) with T,

$$\frac{d^2x}{dT^2}=\frac{dy}{dx}\frac{dx}{dT}\frac{L}{RT^2}-\frac{2yL}{RT^3}+\frac{y}{RT^2}\frac{dL}{dT}$$

$$=\frac{yL}{RT^3}\left\{\frac{dy}{dx}\frac{L}{RT}-2+\frac{T}{L}\frac{dL}{dT}\right\}. \quad \cdots\cdots(8)$$

The value of $\frac{dy}{dx}$ in this equation which will be represented by Y is obtained by differentiating (7) with x as below:

$$\frac{dy}{dx}=Y=\frac{\nu^2(1-x)^2-\nu x^2}{\{\nu(1-x)+x\}^2}. \quad \cdots\cdots\cdots\cdots\cdots\cdots(9)$$

Thus the equation (8) can be expressed as:

$$\frac{d^2x}{dT^2}=\frac{yL}{RT^3}\left\{Y\frac{L}{RT}-2+\frac{T}{L}\frac{dL}{dT}\right\}. \quad \cdots\cdots\cdots(10)$$

The condition for the maximum of $\frac{dx}{dT}$ with temperature variation can be obtained by putting the right hand side of the above equation to zero, and this condition will be employed in the following in discussing the phenomenon of fusion of various substances. As to the values of y and Y corresponding to various values of x for comparatively small values of ν they are already shown in a previous paper[1], and for comparatively high values of 10000, 100000 and 1000000 they are plotted in enlarged scale in curves in Figs. 1 and 2. For very large values of ν y increases almost proportionally with x and Y remains almost constant by taking the value of 1 except the value of x which is very close to 1. When x approximates extremely to 1 y attains a maximum, which corresponds to $Y=0$ in Fig. 2, and then decreases abruptly to

Fig. 1

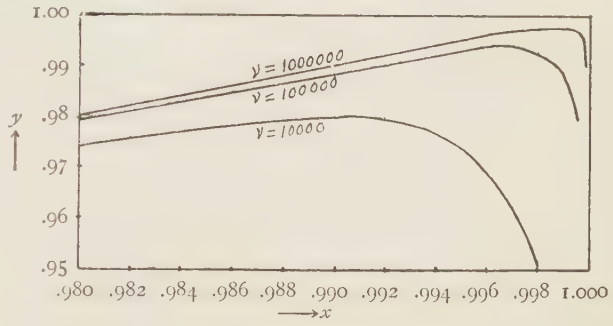
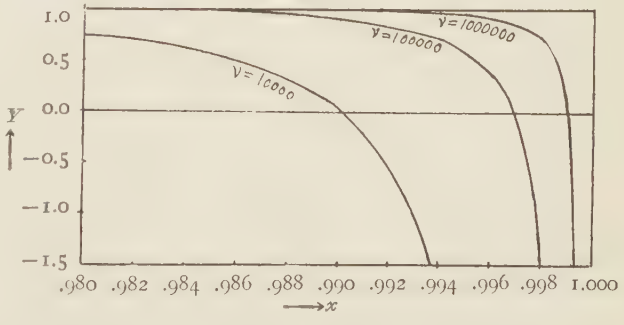


Fig. 2



1. U. Yoshida: *loc. cit.*

zero at $x=1$. The maximum point of y obtained by putting $Y=0$ in equation (9) is

$$1-x=\frac{x}{\nu^{\frac{1}{2}}},\qquad\qquad(11)$$

and from this equation we get for a very large value of ν

$$x=1-\frac{1}{\nu^{\frac{1}{2}}}.\qquad\qquad(12)$$

This shows that the maximum point of y approaches asymptotically to $x=1$ as the value of ν is increased indefinitely. If we take the temperature at which the value of x gives the maximum to y for a very large number of ν as the melting point of the crystal nuclei, then the melting of a crystal composed of an infinite number of constituent molecules comes to occur at $x=1$ corresponding to the perfect decomposition of the crystal into free liquid molecules.

In the previous paper[1] an essentially similar expression of K_c as (4) was used for the equilibrium between the cybotactic crystals and the free liquid molecules, and also between the crystal nuclei and the free liquid molecules. However, the writer made a serious mistake there in calculating the concentration of the cybotactic crystals and the free liquid molecules; and consequently he gave erroneous results to the specific heats of the super-cooled liquids. A correct calculation on this problem will be published in near future. As to the result obtained for the relation between the latent heat of fusion and the melting point of monoatomic elements no correction in essential points seems to be needed, because essentially the same expression of K_c as (4) was employed.

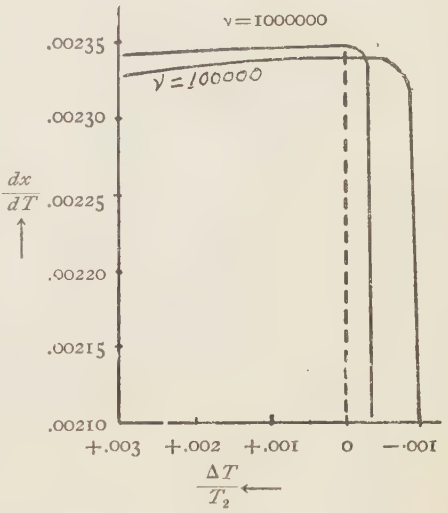
Designation of the Melting Point

The curves drawn in Fig. 3 show the manner of variation of the value of $\frac{dx}{dT}$ of ethyl alcohol with temperature for the values of ν of 100000 and 1000000. In this figure T_2 represents the temperature at which $\frac{dx}{dT}$ is maximum, and ΔT denotes the difference T_2-T for any temperature T. Though the manner of calculation in getting such curves will be explained later, this figure is shown here as an example to show the important behavior of the temperature dependence of

1. *loc. cit.*

$\frac{dx}{dT}$: i. e. the sudden decrease of the value of $\frac{dx}{dT}$ from a certain positive value to zero at a certain temperature for a very large number of ν. The sudden break of the $\frac{dx}{dT}$ curve is due to the presence of the factor y in equation (6), which decreases suddenly to zero from its maximum value at the extreme vicinity of $x=1$ for a very high value of ν. As the occurrence of the nuclear decomposition is due to the presence of the nuclei to be decomposed, such sudden decrease of the value of $\frac{dx}{dT}$ from a certain positive value to zero at a certain temperature signifies that the crystal nuclei can exist only below that temperature and can not exist above it in stable equilibrium. Consequently the melting point of the crystal of a substance can be well designated sharply to take place at a definite temperature where the sudden decrease to zero of the value of $\frac{dx}{dT}$ happens. The maximum point of y, at which arises the sudden decrease of $\frac{dx}{dT}$ for a very high value of ν, can be located to $x=1-\frac{1}{\nu^{\frac{1}{2}}}$ by putting $Y=0$ as is stated before.

Fig. 3
Ethyl alcohol



From the relation between the melting point T_m and the T_2 point, at which happens the maximum of $\frac{dx}{dT}$ for a very great number of ν, various substances can be classified into two kinds: the one having these two temperatures coincident, and the other with which these two temperatures are separated distinctly. As was found in the previous papers almost all of the monoatomic elements except bismuth and gallium belong to the latter kind. Ethyl alcohol of which the temperature dependence of $\frac{dx}{dT}$ is shown in Fig. 3 belongs to the first kind. As is evident in Fig. 3 the T_2 point which is represented by a broken line in the figure is situated very close to the breaking

point of the $\frac{dx}{dT}$ -curve. Moreover the breaking point approaches to the T_2 point with increase of the value of ν, and the final coincidence of these two points for $\nu=\infty$ can be imagined from the curves in the figure.

The Freezing Points of the Solvent and the Solute in a Dilute Solution

Let us apply the above way of reasoning to the crystallization of the solute and the solvent in a dilute solution, and test whether it is consistent or not. Now consider a dilute solution which contains s molecules of a solute in N molecules of a solvent whose freezing point is very low. If we represent respectively by s_f and s_c the numbers of the free molecules and the crystal nuclei of the solute, each one of which is composed of ν molecules, then we have

$$s=s_f+\nu s_c. \quad \cdots\cdots(13)$$

If we define the ratio $\frac{s_f}{s}$ as the degree x of decomposition of the crystal nuclei, then we get

$$x=\frac{s_f}{s}=\frac{s_f}{s_f+\nu s_c} \quad \cdots\cdots(14)$$

and $$1-x=\frac{\nu s_c}{s_f+\nu s_c} \quad \cdots\cdots(15)$$

The molecular concentrations of the free molecules and the crystal nuclei of the solute are respectively

$$\frac{s_f}{N+s_f+s_c}=\frac{sx}{N+s_f+s_c} \text{ and } \frac{s_c}{N+s_f+s_c}=\frac{\frac{s}{\nu}(1-x)}{N+s_f+s_c}, \quad \cdots(16)$$

and consequently the reaction constant K_c for the equilibrium between the free molecules and the crystal nuclei composed of ν molecules becomes

$$K_c=\frac{\left(\frac{sx}{N+s_f+s_c}\right)^{\nu}}{\frac{\frac{s}{\nu}(1-x)}{N+s_f+s_c}}.$$

If we take $N+s_f+s_c \fallingdotseq N$ for the case of dilute solution the above equation can be writen as

$$K_c=\nu\frac{\left(\frac{s}{N}\right)^{\nu}}{\frac{s}{N}}\frac{x^{\nu}}{1-x}. \quad \text{.....(17)}$$

Next let L be the heat of solution per 1 g-mol of the solute in the solvent, and let us suppose that L is approximately independent from temperature, then the integrated form of the reaction isochore becomes

$$\nu\frac{\left(\frac{s}{N}\right)^{\nu}}{\frac{s}{N}}\frac{x^{\nu}}{1-x}=Cc^{-\frac{\nu L}{RT}}, \quad \text{.....(18)}$$

where C is a constant. This is entirely the same form as the equations (4) and (5) for the case of the freezing of a pure solvent, and the same condition for the freezing point, i. e. $1-x=\frac{x}{\nu^{\frac{1}{2}}}$ can be applied to the present case. From (18) we get

$$\frac{\nu^{\frac{1}{\nu}}\frac{s}{N}}{\left(\frac{s}{N}\right)^{\frac{1}{\nu}}}\frac{x}{(1-x)^{\frac{1}{\nu}}}=C^{\frac{1}{\nu}}e^{-\frac{L}{RT}}. \quad \text{.....(19)}$$

By taking $\nu^{\frac{1}{\nu}}=\left(\frac{s}{N}\right)^{\frac{1}{\nu}}=1$ for a very large number of ν, and

$$\frac{x}{(1-x)^{\frac{1}{\nu}}}=\frac{x\nu^{\frac{1}{2\nu}}}{x^{\frac{1}{\nu}}}=1$$

by applying the condition of the freezing point for a very large number of ν, the equation (19) becomes

$$\frac{s}{N}=C^{\frac{1}{\nu}}e^{-\frac{L}{RT}}. \quad \text{.....(20)}$$

This equation represents the relation between the molar concentration $c=\frac{s}{N}$ of the solution and the limiting temperature at which the crystallization of the solute commences. Thus this is nothing but the relation between the temperature and the solubility expressed in molar concentration of a solute in a solution. By expressing in logarithmic form we get the expression of the dependence of the solubility upon the temperature:

$$\log c=-\frac{L}{RT}+A, \quad \text{.....(21)}$$

where A is a constant.

Next let us consider the case of the freezing of the solvent in a dilute solution. If we represent by N_f and n_c respectively the number of the free molecules and that of the crystal nuclei among the total number N of the solvent molecules as before, and if we define $\frac{N_f}{N_f+n_c}$ as the degree of decomposition x of the crystal nuclei, then we have

$$\frac{N_f}{N_f+n_c}=x, \quad \frac{n_c}{N_f+n_c}=1-x,$$

and

$$K_c=\left\{\frac{(N_f+n_c)x}{N_f+n_c+s}\right\}^{\nu} \div \frac{(N_f+n_c)(1-x)}{N_f+n_c+s},$$

where s represents the number of the solute molecules. As the crystal nuclei can not exist at the temperatures higher than the freezing point of the solvent, and begin to be formed at the freezing point, we can regard N_f+n_c as constant and equal to the total number of solvent molecules N above the freezing point. Thus if we represent $(N_f+n_c)/(N_f+n_c+s)=N\div(N+s)$ by p, and consider it to be constant, then the integrated form of the reaction isochore becomes

$$K_c=\frac{(px)^{\nu}}{p(1-x)}=Cc^{-\frac{\nu L}{RT}},$$

$$\text{i. e.} \quad \frac{px}{p^{\frac{1}{\nu}}(1-x)^{\frac{1}{\nu}}}=C^{\frac{1}{\nu}}e^{-\frac{L}{RT}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots(22)$$

by assuming that L is approximately constant. By taking $1-x=\frac{x}{\nu^{\frac{1}{2}}}$ which is the condition for freezing, and $p^{\frac{1}{\nu}}=1$ for a very large number of ν, we get from (22)

$$p=\frac{N}{N+s}=C^{\frac{1}{\nu}}e^{-\frac{L}{RT}}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(23)$$

Next if we put $s=0$ the equation becomes

$$1=C^{\frac{1}{\nu}}e^{-\frac{L}{RT_m}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots(24)$$

in which T_m represents the freezing point of the pure solvent. From (23) and (24) we get

$$\frac{N}{N+s}=e^{-\frac{L}{R}\left(\frac{1}{T}-\frac{1}{T_m}\right)} \fallingdotseq e^{-\frac{L}{RT_m^2}(T_m-T)}.$$

If we represent T_m-T by ΔT, which is the lowering of the freezing point of the solvent in a dilute solution, and $\frac{s}{N}$ by c the molar con-

centration of solute in a dilute solution, then we get

$$1-\frac{s}{N}=1-\frac{L}{RT_m^2}\Delta T,$$

$$\text{i. e.}\quad \Delta T=\frac{s}{N}\frac{RT_m^2}{L}=c\frac{RT_m^2}{L}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(25)$$

This is the well known expression for the lowering of the freezing point of the solvent in a dilute solution.

As the concordant results deduced as above by our mode of reasoning can be considered to be a confirmation of its correctness, we shall apply it in the following to the phenomena of crystallization of various substances which are provided with necessary data.

Crystallization of Elements and Compounds

Ordinarily the latent heat of fusion of the crystal of a substance is confined to that at its melting point. However when we want to discuss the thermal equilibrium between the free molecules and the crystal nuclei in the super-cooled state of a substance, we must know the value of the latent heat of fusion of the crystal nuclei at various temperatures. If we take the latent heat of fusion of the crystal nuclei to be the same as that of the adult crystal of the same substance by considering the number of constituent molecules of a crystal nucleus to be sufficiently large, then the latent heat of fusion L at a temperature T will be obtained approximately by the following equation from the values of the latent heat of fusion L_m, the specific heats C_p and c_p of the liquid and the adult crystal at the melting point T_m by neglecting the variation of (C_p-c_p) with temperature.

$$L=L_m+(C_p-c_p)(T-T_m). \quad \ldots\ldots\ldots\ldots\ldots\ldots(26)$$

With this equation we get

$$\frac{dL}{dT}=C_p-c_p. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(27)$$

By representing C_p-c_p by a, and by putting the values of L and $\frac{dL}{dT}$ given by (26) and (27) in equation (10), the condition of the maximum of $\frac{dx}{dT}$ becomes

$$Y\frac{L_m+a(T_2-T_m)}{RT_2}-2+\frac{T_2}{L_m+a(T_2-T_m)}a=0, \ldots(28)$$

where T_2 represents the temperature at which the maximum of $\frac{dx}{dT}$

takes place. When the maximum of $\frac{dx}{dT}$ happens at a temperature T_2 which is distinctly lower than T_m, the value of the degree of decomposition x of the crystal nuclei at the temperature T_2 must be definitely smaller than 1, because the perfect decomposition happens at the melting point T_m which is distinctly higher than T_2. As the value of Y remains 1 for a very large value of ν and for all the values of x except the extreme vicinity of 1 where it decreases abruptly, the value of Y should be taken to be $Y=1$ in the present case where T_2 is distinctly lower than T_m. Thus by putting $Y=1$ the equation (28) becomes

$$\frac{L_m+a(T_2-T_m)}{RT_2}-2+\frac{RT_2}{L_m+a(T_2-T_m)}\frac{a}{R}=0$$

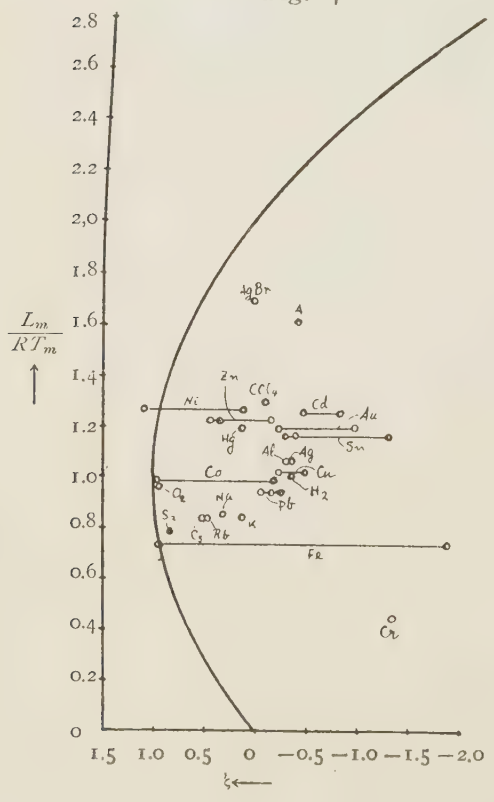
By representing $\frac{a}{R}$ by ξ we get from this equation

$$\frac{L_m+R\xi(T_2-T_m)}{RT_2}=1\pm\sqrt{1-\xi} \quad \ldots\ldots(29)$$

With this equation the value of T_2 can be calculated when the values of L_m, T_m and a for a substance is known. It is clear from equation (29) that for the value of T_2 to be different distinctly from T_m the value of ξ should be not greater than 1. Another condition which must be satisfied to conform with our way of reasoning is that T_2 must not exceed T_m. Consequently the limiting case for this condition will be found by taking $T_2=T_m$ in equation (29) as follows:

$$\frac{L_m}{RT_m}-1=\pm\sqrt{1-\xi}$$

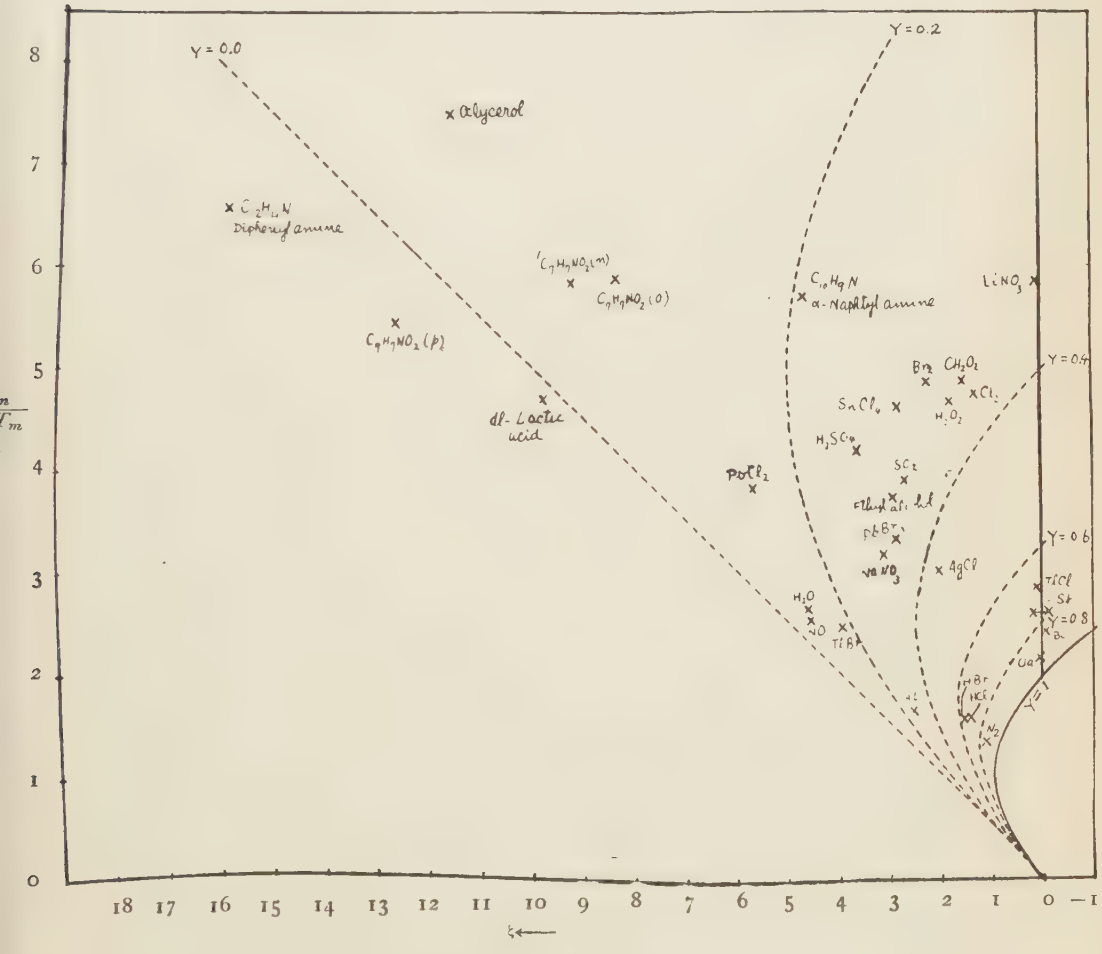
Fig. 4



$$\text{i. e.} \quad \left(\frac{L_m}{RT_m} - 1\right)^2 = 1 - \xi. \quad \text{.....(30)}$$

This boundary relation between L_m/RT_m and ξ, within which the situation of a substance refering to its values of L_m/RT_m and ξ must be confined in order to have the value of T_2 smaller than T_m, is represented by the parabola in Figs. 4 and 5. In these figures the situations of various substances as regard to the values of L_m/RT_m and ξ, which are taken as ordinates and abscissae respectively, are shown by small circles and crosses, by being distinguished according as they are confined or not in the parabolic domain.

Fig. 5



Most of the data necessary in our computation are taken from International Critical Table and are compiled in Tables I and II. As to the values of the difference of the specific heats $C_p - c_p$ of the elements, measurements on some substances which are considerably different according to the authors were compiled in International Criti-

Table I

Substance	Melting point T_m in °K	Heat of fusion L_m in $\frac{\text{Cal}}{\text{g-mol}}$	$\frac{L_m}{RT_m}$	Specific heat C_p in $\frac{\text{cal}}{\text{g-mol}}$ (liquid)	Specific heat c_p in $\frac{\text{cal}}{\text{g-mol}}$ (solid)	$\frac{C_p - c_p}{R}$
A	84°	268.0	1.61	5 35	6.18	−0.418
Ag*	1234°	2625.	1.07	—	—	−0.34
Al*	933°	1910	1.07	—	—	−0.30
Au*	1336°	3180	1.20	—	—	−0.22 −0.99
Cd*	594°	1480	1.258	—	—	−0.48 −0.83
Co*	1753°	3440	0.988	—	—	+1.0 −0.18
Cr*	1888°	1650	0.441	—	—	−1.33
Cs	299°	501	0.845	7.92	6.92	+0.51
Cu*	1355°	2750	1.021	—	—	−0.22 −0 50
Fe*	1808°	2680	0.746	—	—	+0.97 −1.86
Hg	234°	556	1.196	6.95	6.67	+0.14
K	335°	569	0.855	7.16	6.93	+0.115
Na	371°	633	0.860	7.40	6.78	+0.31
Ni*	1725°	4340	1.270	—	—	+1.1 +0.12
Pb*	601°	1123	0.941	—	—	−0.055 −0.145 −0.19
Rb	312°	521	0.840	7.76	0.85	+0.46
Sn*	505°	1670	1.665	—	—	−0.28 −0.37 −1.3
Zn*	693°	1695	1.225	—	—	+0.46 +0.36 −0.15
H_2	14°	28.2	1.013	0.466	1.146	−0.343
O_2	55°	105 o	0.961	12.60	10.72	+0.947
S_2	386°	600	0.783	14.5	12.8	+0.856
AgBr	703°	2365	1.69	14.3	14.3	0.0
CCl_4	249°	641	1.30	30.8	30.96	−0.078

Table II.

Substance	Melting point T_m in °K	Heat of fusion L_m in cal / g-mol	$\frac{L_m}{RT_m}$	Specific heat C_p in cal / g-mol (liquid)	Specific heat c_p in cal / g-mol (solid)	$\frac{C_p - c_p}{R}$ in cal / g-mol	γ
Bi*	544°	2602	2,41	—	—	−0.024 −0.18	0.834 0.861
Ga	303°	1324	2.205	5.49	5.49	0.0	0.907
Sb*	904°	4660	2.60	—	—	+0.44 −0.084	0.705 0.782
Br_2	266°	2580	4.89	17.18	12.8	+2.21	0.317
Cl_2	171°	1624	4.77	16.0	13.4	+1.31	0.361
I_2	387°	4000	5.20	13.4(?)	13.3	+0.050(?)	0.383(?)
N_2	63°	170	1.36	13.28	10.98	+1.16	0.844
HCl	159°	505	1.60	14.86	11.95	+1.47	0.676
HBr	186°	576	1.56	14.5	11.4	+1.56	0.641
HI	220°	726	1.66	16.4	11.35	+2.55	0.28
NO	110°	555	2·54	17.4	8.46	+4.51	0.089
H_2O	273°	1433	2.65	18 0	8.85	+4.62	0.098
H_2O_2	271°	2503	4.66	19.6	16.0	+1.84	0.344
SO_2	243°	1900	3.94	20.0	14.65	+2.71	0.334
H_2SO_4	283.4°	2360	4.20	33.75	26.45	+3.66	0.268
$SnCl_4$	240°	2190	4.60	38.6	32.9	+2.89	0.298
$PbCl_2$	758°	5800	3.85	33.63	22.22	+5.70	0.125
$PbBr_2$	771°	5140	3.36	20.8	15.0	+2.90	0.338
TlCl	700°	3970	2.86	14.15	13.85	+0.145	0.677
TlBr	733°	3610	2.48	22.70	14,93	+3.92	0.169
AgCl	724°	4400	3.06	18.45	14.45	+2.02	0.437
$LiNO_3$	523°	6090	5.86	26.90	26.70	+0.104	0.338
$NaNO_3$	606°	3850	3.20	36.6	30.4	+3.09	0.324
CH_2O_2(Formic acid)	281°	2710	4.87	22.8	19.8	+1.53	0.346
C_2H_6O(Ethyl alcohol)	159°	1188	3.76	20.7	14.93	+2.91	0.327
$C_3H_8O_3$(Glycerol)	292°	4370	7.49	52.4	31.3	+10.63	0.079
$C_3H_6O_3$(*dl*-Lactic acid)	290°	2710	4.71	49.8	30.36	+9 80	−0.016
$C_7H_7NO_2$ (*o*-Amino benzoic acid)	418°	4870	5.87	71.9	55.3	+8.32	0.101
$C_7H_7NO_2$ (*m*-Amino benzoic acid)	453°	5220	5.81	71.9	53.5	+9.24	0.071
$C_7H_7NO_2$ (*p*-Amino benzoic acid)	461°	5000	5.47	73.3	48.2	+12.67	−0.058
$C_{10}H_9N$ (α-Naphtyl amine)	323°	3660	5.71	87.0	77.8	+4.70	0.206
$C_{12}H_{11}N$ (Diphenyl amine)	326.4°	4260	6.58	104.5	73.1	+15.84	−0.062
$C_{16}H_{32}O_2$ (Palmitic acid)	328°	10070	15.48	209	137.5	+36.1	−0.022

cal Table. Though these measurements are not reliable they are tabulated in Tables I and II by being marked by * for these substances, and these substances are also plotted in Figs. 4 and 5. When the situation of a substance in the figures is different for different values of $(C_p-c_p)/R$ the different situations are connected by a horizontal line indicating that they belong to a same substance. The substances which are provided with reliable values of C_p and c_p are water, mercury, ethyl alcohol, glycerol and *dl*-lactic acid; and they are also tabulated and plotted in Tables I and II and in Figs. 4 and 5. For the other substances the specific heats C_p and c_p have not been measured just at the melting point. But there are some for which the specific heats C_p and c_p are measured respectively at the temperatures not much far off the melting point; and these substances, though accompanied by considerable errors, are tabulated and plotted in the tables and the figures respectively. In Fig. 4, only the substances whose situations are confined within the parabolic domain are represented, and in Fig. 5, only those situated outside the parabolic domain are shown in reduced scale.

It is especially note-worthy that all substances which are situated within the parabolic domain have the values of L_m/RT_m smaller than 2. For the positive value of ξ which is smaller than 1 this must be satisfied in order that the temperature T_2 be lower than T_m. However, the circumstances are different for the negative values of ξ; and L_m/RT_m can take the values higher than 2 even within the parabolic domain. In spite of this possibility of L_m/RT_m being greater than 2, it remains always smaller for all the substances in the parabolic domain, which consist mostly of monoatomic elements. According to the writers's view, the main cause for this is probably erroneous measurements or erroneous estimations of the specific heats C_p and c_p at the melting point. As is stated above no reliance on the values of C_p-c_p must be put for all the substances situated in the parabolic domain except Hg. Ordinarily the specific heat of a solid is measured with polycrystalline material. As is imagined in a former paper[1] the crystalline boundaries are cemented by the super-cooled liquid or solid of the same substance, and the width of this boundary liquid layer increases with rise of the temperature. This signifies a partial melting of the crystals at their boundary liquid layer which increases as the tempera-

1. U. Yoshida: These Memoirs, **24** (1943); 學術研究會議編物理學講演集 **4**, (昭 18).

ture approaches to the melting point. This fact will assist in giving a value higher than the ideal one of the specific heat of a solid near the melting point. Thus if we assume, ideally speaking, that the value of the specific heat of a solid can not exceed that of the liquid of the same substance at the melting point at least for the monoatomic elements, then it follows that the value of L_m/RT_m should be smaller than 2 in order to cause the melting of the crystal at a temperature which is definitely higher than the T_2 point. This is nothing but the T_2-point law deduced by taking approximately $\xi=0$ in previous papers as being valid for most of the monoatomic elements except bismuth and gallium. Besides the monoatomic elements, five substances H_2, O_2, S_2, AgBr and CCl_4 obey also the T_2-point law as is seen in Fig. 4.

Next let us consider the substances which are situated outside the parabolic domain. For a substance situated in the parabolic domain the maximum of $\frac{dx}{dT}$ occurs with $Y=1$ as is stated above. The maximum of $\frac{dx}{dT}$ can also takes place with the values of Y which are definitely smaller than 1. But for a very great number of ν, Y can take a value which is distinctly smaller than 1 only at the limit when x tends to 1. As the melting point is also designated at the same limit, the T_2 point becomes thus coincident with the melting point T_m in the present case. Consequently by putting $T_2=T_m$ in equation (28), we get

$$Y\frac{L_m}{RT_m}-2+\frac{RT_m}{L_m}\xi=0,$$

$$\text{or}\qquad Y=\left(2-\frac{RT_m}{L_m}\xi\right)\frac{RT_m}{L_m}. \qquad \text{.....(31)}$$

The value of Y calculated by this equation for various substances are tabulated in the last column of Table II. The curves drawn in broken line in Fig. 5 show the relation between L_m/RT_m and ξ for various constant values of Y, i. e. for $Y=0$, .2, .4, .6 and .8; and they represent the situation of the substances as regard to the value of Y. As the peculiarity of the substances situated outside the parabolic domain is that they have the T_2 points which are coincident respectively with their melting points T_m, this will be called "the coincident T_2-T_m points law."

Considering in the above way, all substances including elements and compounds can be divided with respect to their crystallizing or melting property into two kinds: the one those obeying the T_2 point

law, and the other those governed by the coincident $T_2 - T_m$ points law. Most of the monoatomic elements, of which L_m/RT_m is smaller than 2, obey the former law; and most of the compounds including inorganic and organic ones obey the latter law. As is seen from Fig. 5 the value of ξ is positive for all the compounds, indicating that the specific heat in the liquid state is greater than that in the crystalline state at the melting point. This seems to be caused by the setting up of new degree of freedom of thermal motion by the melting. It is also very interesting to note in Fig. 5 that the situation of all the substances belonging to the coincident $T_2 - T_m$ points law is not only bounded by the straight line $\xi = 0$, but is almost bounded also by the other straight line $Y = 0$. This indicates that a further approach to the limit $x = 1$ than that corresponding to $Y = 0$, $\left(\text{i. e. } 1 - x = \frac{x}{\nu^{\frac{1}{2}}}\right)$ for a very large number of ν is not necessary in causing the melting of the crystal of a substance. For the organic compounds having high molecular weight, both the values of L_m/RT_m and ξ become considerables in general; and with palmitic acid having the molecular weight of 256 they are so large as 15.48 and +36.1 respectively that this substance escaped far from the scope of Fig. 5.

Till now we have considered that the temperature T_2 at which the maximum of $\frac{dx}{dT}$ takes place coincides with the melting point T_m of the substance when Y becomes definitely smaller than 1 for a very great number of ν. This is of course an approximation for a finite number of ν, however great it may be, as we have defined the melting to take place at $Y = 0$ $\left(1 - x = \frac{x}{\nu^{\frac{1}{2}}}\right)$. However, this approximation is well allowable if we take the value of ν sufficiently great, as is shown in the following by taking the case of ethyl alcohol as an example.

From the necessary data given in Table II for ethyl alcohol we get the value of Y as $Y = 0.327$ with equation (31); and for this value of Y, the values of x becomes 0.9962 and 0.9988 respectively for $\nu = 100{,}000$ and $\nu = 1000{,}000$. If we call the temperature at which Y and x take these values respectively as "the T_2 point," then the latent heat of fusion L can be expressed, by taking T_2 as almost the same as T_m the real melting point at which Y becomes zero, as follows:

$$L = L_m + a(T - T_2)$$

By using this value of L the equation (5) becomes on integration

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = Ce^{-\frac{L_m - aT_2}{RT} + \frac{a}{R}\log T}, \quad \cdots\cdots\cdots\cdots(32)$$

where C is a constant. Next if we represent the value of x at the temperature T_2 by x_2, then we get from equation (32)

$$\frac{x_2}{(1-x_2)^{\frac{1}{\nu}}} = Ce^{-\frac{L_m - aT_2}{RT_2} + \frac{a}{R}\log T_2}. \quad \cdots\cdots\cdots\cdots(33)$$

By dividing (32) by (33) we have

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = \frac{x_2}{(1-x_2)^{\frac{1}{\nu}}} e^{-\frac{L_m - aT_2}{R}\left(\frac{1}{T} - \frac{1}{T_2}\right) + \frac{a}{R}\log\frac{T}{T_2}}. \quad \cdots(34)$$

If we represent $T_2 - T$ by ΔT, and consider it to be very small when compared with T_2, then (34) becomes, by expanding into the power series of $\Delta T/T_2$, as follows:

$$\frac{x}{(1-x)^{\frac{1}{\nu}}} = \frac{x_2}{(1-x_2)^{\frac{1}{\nu}}}\left\{1 - \frac{L_m}{RT_2}\frac{\Delta T}{T_2}\right\}. \quad \cdots\cdots\cdots(35)$$

Similarly we get from equation (6)

$$\frac{dx}{dT} = \frac{y}{T_2}\left\{\frac{L_m}{RT_2} + \left(2\frac{L_m}{RT_2} - \xi\right)\frac{\Delta T}{T_2}\right\}. \quad \cdots\cdots\cdots(36)$$

By taking, as for the case of ethyl alcohol, $T_2 = T_m = 159°\mathrm{K}$, $L_m/RT_2 = L_m/RT_m = 3.76$, $\xi = +2.91$, $x_2 = 0.9962$ for $\nu = 100{,}000$ and $x_2 = 0.9988$ for $\nu = 1000{,}000$, the values of $\frac{dx}{dT}$ for different values of $\Delta T/T_2$ were calculated with equations (35) and (36). In carring out the calculation, the values of x corresponding to various values of $\Delta T/T_2$ were first obtained with equation (35), then the values of y corresponding to the values of x which again correspond to the various values of $\Delta T/T_2$ were found by the aid of Fig.1, and lastly the values $\frac{dx}{dT}$ for different values of $\Delta T/T_2$ were calculated from equation (36) by using the values of y thus calculated. The results of calculation for $\nu = 100{,}000$ and $\nu = 1000{,}000$ are shown by Fig.3. As is seen in the figure the value of $\frac{dx}{dT}$ drops suddenly to zero at a certain temperature which corresponds to the melting point according to our definition and is slightly different from the T_2 point. However, as T_m approaches very rapidly to T_2 when ν increases from 100,000 to 1000,000, we can say that T_2 coincides with the melting point T_m at the limit when ν tends to infinity.

Lastly it must be noted that the cost of this research has been defrayed from the Scientific Research Expenditure of the Department of Education.

Structural Relaxation of Amorphous Solids and the Cybotactic Structure of Super-cooled Liquids

By

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Abstract

A sudden increase of the specific heat of an amorphous solid in its softening temperature range was considered to be caused by the dissolution of molecular aggregates, each composed of a considerable number of molecules, into free liquid molecules, and the temperature dependence of the specific heats of glycerol, ethyl alcohol and *dl*-lactic acid was found to be in good accord with that calculated by applying van't Hoff's reaction isochore to the decomposition of the molecular aggregates into free liquid molecules. As to the specific heats of these substances in their super-cooled liquid state above the softening temperature range, the previous wrong calculation on the decomposition of the cybotactic groups into free liquid molecules is revised. The general tendency of the temperature dependence of the specific heat of an amorphous substance in and above the softening temperature range is thus well understood by the presence of two kinds of molecular aggregates: the one composed of an immense number of molecules and the other the cybotactic group of only a small number of constituent molecules.

Introduction

A cybotactic theory of amorphous solids and supercooled liquids was proposed by the writer in previous papers.[1] In that theory the amorphous solid and the super-cooled liquid of a substance were considered to consist of free molecules of the substance and the cybotactic groups having the size of the order of the unit cell of the crystal. The cybotactic groups have no permanent stability. They are formed and decomposed spontaneously here and there in the liquid. The proportion in equilibrium of the total number of the cybotactic groups in reference to the total number of the free molecules is determined by the temperature, and it increases with decreasing temperature. When the temperature is lowered below the solidifying point of a substance,

1. U. Yoshida: These Memoirs, A, **23**, 207, 233 (1941)

without causing crystallization, it becomes supercooled. On further cooling the substance gets increasingly viscous; and at last it attains the glassy state or the state of amorphous solid, which is supposed to contain a considerable amount of cybotactic groups. The transformation from the amorphous solid to the super-cooled liquid state or *vice versa* takes place in the softening temperature range, and this transformation is accompanied by a remarkable sudden change in various physical properties of the substance, though it is not so sharp as in the case of melting of a crystal. In a paper[1] recently published the writer regarded the softening of an amorphous solid as the relaxation of the cybotactic structure of the substance; and by considering that the proportion between the numbers of the cybotactic groups and the free liquid molecules of a substance is in equilibrium above the softening temperature range, the contribution to the specific heat of the amount of heat required to decompose the cybotactic groups on raising the temperature was calculated with glycerol, ethyl alcohol and *dl*-lactic acid by applying van't Hoff's reaction isochore. However, as was already noticed,[2] the writer made a serious mistake there in calculating the concentration of the cybotactic groups and the free liquid molecules. Hence the calculation is revised and is described in the following, together with a similar calculation in the softening temperature range by considering the softening as due to the decomposition of the molecular aggregates each consisting of such a considerable number of molecules as about 200 into free liquid molecules.

Temperature Dependence of the Proportion of Free Liquid Molecules

Let the numbers of the free liquid molecules and of the cybotactic groups among the total number N of the molecules in a supercooled liquid of a substance be N_f and n_c respectively. If we represent by ν the number of the constituent molecules of a cybotactic group we have:

$$N = N_f + \nu n_c. \quad \text{.....(1)}$$

Let us define the ratio x of the number of free molecules and the number of the total discrete particles which is equal to the sum of N_f and n_c as the degree of decomposition of the cybotactic groups. Then we get:

1. U. Yoshida: These Memoirs, A, **24**, 1 (1942)
2. U. Yoshida: These Memoirs, A, (1943)

$$x=\frac{N_f}{N_f+n_c}, \quad \ldots\ldots(2)$$

and

$$1-x=\frac{n_c}{N_f+n_c}, \quad \ldots\ldots(3)$$

and the reaction constant K_c becomes:

$$K_c=\frac{\left(\frac{N_f}{N_f+n_c}\right)^{\nu}}{\frac{n_c}{N_f+n_c}}=\frac{x^{\nu}}{1-x}. \quad \ldots\ldots(4)$$

If we represent by T the absolute temperature, by R the gas constant refering to one gram mol, by M the molecular weight of a substance and by L the heat of decomposition of the cybotactic groups per one gram; then the reaction isochore takes the form:

$$\frac{d\log K_c}{dT}=\left(\frac{\nu}{x}+\frac{1}{1-x}\right)\frac{dx}{dT}=\frac{\nu(1-x)+x}{x(1-x)}\frac{dx}{dT}$$

$$=\frac{\nu ML}{RT^2} \quad \ldots\ldots(5)$$

for a constant value of ν. From equation (5) we have:

$$\frac{dx}{dT}=\frac{\nu x(1-x)}{\nu(1-x)+x}\frac{ML}{RT^2}. \quad \ldots\ldots(6)$$

The heat of decomposition L of the cybotactic groups changes with temperature. If we represent by L_c the heat of decomposition at the temperature T_c and by $(C_f-C_c)_c$ the difference between the specific heats of the free liquid molecules and the cybotactic groups refering to one gram at the same temperature, then the heat of decomposition L at a temperature T will be given approximately for a temperature range not very much wide by:

$$L=L_c+(C_f-C_c)_c(T-T_c). \quad \ldots\ldots(7)$$

Thus if we put this value of L into equation (5) we get, on integration:

$$K_c=\frac{x^{\nu}}{1-x}=Ce^{-\frac{\nu M\{L_c-(C_f-C_c)_cT_c\}}{RT}+\frac{\nu M}{R}(C_f-C_c)_c\log T},$$

or

$$\frac{x}{(1-x)^{\frac{1}{\nu}}}=C^{\frac{1}{\nu}}e^{-\frac{M\{L_c-(C_f-C_c)_cT_c\}}{RT}+\frac{M}{R}(C_f-C_c)_c\log T} \quad \ldots\ldots(8)$$

If we represent the degree of cybotactic decomposition at the temperature T_c by x_c, equation (8) becomes:

$$\frac{x_c}{(1-x_c)^{\frac{1}{\nu}}}=C^{\frac{1}{\nu}}e^{-\frac{M\{L_c-(C_f-C_c)_c T_c\}}{RT_c}+\frac{M}{K}(C_f-C_c)_c \log T_c} \quad \cdots\cdots(9)$$

Hence by combining equations (8) and (9) we obtain:

$$\frac{x}{(1-x)^{\frac{1}{\nu}}}=\frac{x_c}{(1-x_c)^{\frac{1}{\nu}}}e^{-\frac{M}{R}\{L_c-(C_f-C_c)_c T_c\}\left(\frac{1}{T}-\frac{1}{T_c}\right)+\frac{M}{R}(C_f-C_c)_c \log\frac{T}{T_c}} \quad \cdots\cdots(10)$$

Next the relation between x and the proportion of the number N_f of free molecules to the total number N of molecules becomes by eliminating n_c from equations (1) and (2):

$$\frac{N_f}{N}=\frac{x}{\nu(1-x)+x}. \quad \cdots\cdots(11)$$

Differentiating equation (11) with respect to T we get:

$$\frac{1}{N}\frac{dN_f}{dT}=\frac{\nu}{\{\nu(1-x)+x\}^2}\frac{dx}{dT},$$

and by using equation (6) this reduces to:

$$\frac{1}{N}\frac{dN_f}{dT}=\frac{\nu^2 x(1-x)}{\{\nu(1-x)+x\}^3}\frac{ML}{RT^2}=y'\frac{ML}{RT^2}, \quad \cdots\cdots(12)$$

where y' represents

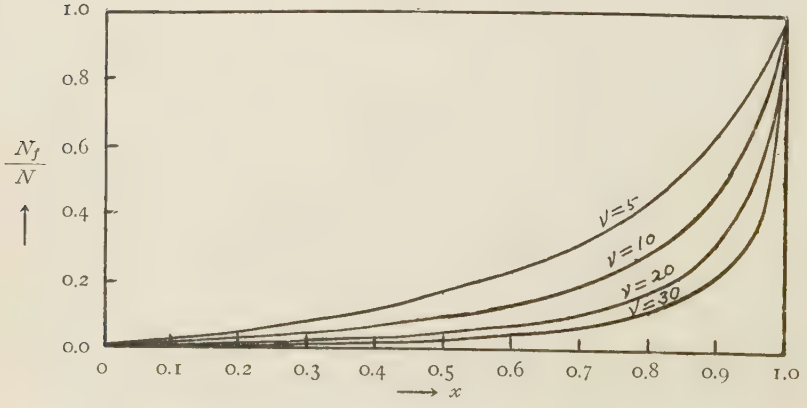
$$y'=\frac{\nu^2 x(1-x)}{\{\nu(1-x)+x\}^3}. \quad \cdots\cdots(13)$$

Hence the heat quantity C_d required to decompose the cybotactic groups in one gram of the substance in raising the temperature by one degree is given by

$$C_d=L\left(\frac{1}{N}\frac{dN_f}{dT}\right)=y'\frac{ML^2}{RT^2}. \quad \cdots\cdots(14)$$

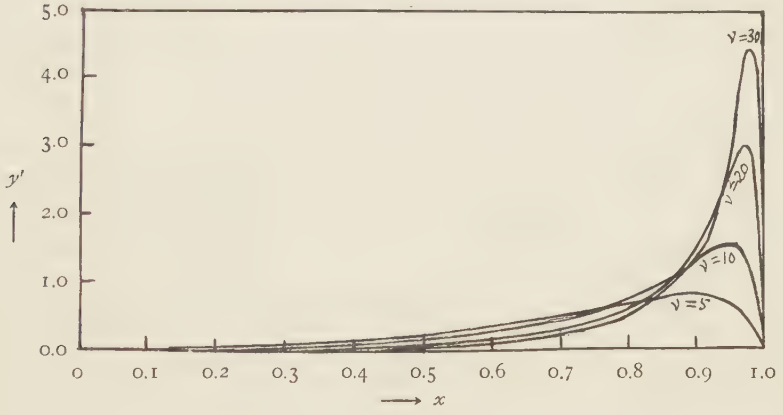
In the following calculations the numerical values of $x/(1-x)^{\frac{1}{\nu}}$,

Fig. 1



N_f/N and y' for various values of ν and x are required, and these relations are represented in graphs. Some of such graphs for comparatively low values of ν are represented as examples in Figs. 1 and 2, to show the general tendency of the dependence of the values of N_f/N and y' upon ν. The variation of the values of N_f/N and y' with x becomes more rapid with increase of the value of ν. When ν tends to infinity in the case of the melting of the adult crystal of a substance the values of y' and N_f/N remain zero at all values of x except at the extreme vicinity of $x=1$, where N_f/N increases abruptly to 1 and y' attains the maximum of infinity and drops suddenly to zero at $x=1$.

Fig. 2



Cybotactic Decomposition in the Super-cooled Liquid State

The substances of which the specific heats were measured at various temperatures both in their crystalline and super-cooled amorphous states are glycerol, ethyl alcohol and *dl*-lactic acid as is stated before. The temperature variation of the specific heats refering to one gram of these substances are shown in Figs. 3, 4, 5 and 6. In these figures the curves drawn in full line refer to the super-cooled liquid and the amorphous solid state, and those drawn in broken line represent the specific heats in the crystalline state. The specific heat curves for the crystalline state run almost linearly with temperature, and those for the super-cooled liquid and the amorphous solid rise very rapidly in the softening temperature range.

The specific heat of a substance in its super-cooled liquid state

may be considered to consist of three parts: 1) The specific heat C_c of the cybotactic groups, which we shall consider to be roughly the same as that of the adult crystal at the same temperature. 2) The specific heat C_f of the free molecules which is supposed to be larger than C_c as will be imagined from the value of the specific heat of the liquid at the melting point where almost all the molecules are likely to be in the free state and not in the state of cybotactic configuration. 3) The heat C_d required for the decomposition of the cybotactic groups in raising the temperature. The temperature dependence of C_f is not obvious. However, as almost all the molecules are likely to be in the free state at the melting point of the adult crystal as was stated before, the specific heat observed for the liquid at this temperature may be taken approximately as that of free molecules. Thus, though it may be rough, the writer assumes that the ratio C_f/C_c remains the same for all temperatures below the melting point and is equal to that of the liquid and the adult crystal at the melting point of the latter; and the value C_f at any temperature is calculated from the value of the specific heat of the adult crystal at the same temperature, which is considered to be approximately the same as C_c.

In the softening temperature range of an amorphous solid its structural relaxation takes place as was stated before, and at the temperatures above that range the substance behaves as liquid by being super-cooled below its melting point. Thus by considering that the super-cooled liquid state is in cybotactic equilibrium we shall apply van't Hoff's reaction isochore as was described before to this case.

In carrying out the numerical calculation of the spcific heat we must select to begin with the reference temperature T_c at which the values of x, L, C_f and C_c for a certain value of ν must be determined. The writer took the temperature just above the softening temperature range as such reference temperature; and its value for ethyl alcohol, glycerol and *dl*-lactic acid are given in Tables II and III. In Table I the molecular weight and the melting point of these substances are tabulated together with the latent heat of fusion at the melting point. When the reference temperature T_c is determined as above, the specific heats C_f and C_c of the free liquid molecules and the cybotactic groups and their difference $(C_f - C_c)_c$ at this temperature can be calculated easily from the specific heat in the crystalline state at the same temperature by using the rough assumption described before. Thus once the value of the heat of decomposition L_c of the cybotactic groups

at the temperature T_c is known the heat of decomposition L of the cybotactic groups at any temperature T can be approximately obtained by equation (7). In order to know the value of L_c the number ν of the constituent molecules of a cybotactic group and the degree of decomposition x_c of the cybotactic groups at the temperature T_c must be determined. However such determination of the values of ν and x_c can not be made uniquely, and the only way in doing this is, though troublesome, repeated trials. If we assign provisionally a certain value to x_c for a given value of ν, then we can find the values of $x_c/(1-x_c)^{\frac{1}{\nu}}$ y' and $(N_f/N)_c$ from the graphs prepared previously. Next from the values of the specific heats C_f and C_c of the free liquid molecules and the cybotactic groups at the temperature T_c as is determined in the way stated before the part C_m of the specific heat of the liquid at the temperature

Table I

	Molecular weight M	Melting point T_m in °K	Heat of fusion at T_m in cal/g
Ethyl alcohol	46	159	25.8
Glycerol	92	292	47.5
dl-Lactic acid	90	290	30.1

Table II

	Structural relaxation				Cybotactic decomposition					
	ν	T_r in °K	x_r	L_r in $\frac{\text{cal}}{\text{g}}$	ν	T_c in °K	x_c	L_c in $\frac{\text{cal}}{\text{g}}$	$(C_f-C_c)_c$ in cal/g	$\left(\frac{N_f}{N}\right)_c$ at T_c
Ethyl alcohol	200	96	0.9975	1.625	5	102	0.93	8.02	0.09	0.726
Glycerol	200	185	0.9975	1.95	5	192	0.97	10.66	0.163	0.865
dl-Lactic acid	200	208	0.9975	2.32	5	215	0.97	12.54	0.172	0.865

Table III

Glycerol

ν	T_c in °K	x_c	L_c in $\frac{\text{cal}}{\text{g}}$	$\left(\frac{N_f}{N}\right)_c$ at T_c	$(C_f-C_c)_c$ in $\frac{\text{cal}}{\text{g}}$
10	190	0.98	7.18	0.83	0.159
5	192	0.97	10.66	0.865	0.163
2	192	0.927	16.4	0.865	0.163

T_c which is required merely to raise the temperature by one degree of the free liquid molecules and the cybotactic groups without causing the cybotactic decomposition will be obtained by

$$C_m = C_f\left(\frac{N_f}{N}\right)_c + C_c\left\{1-\left(\frac{N_f}{N}\right)_c\right\}, \quad \text{.....(15)}$$

and the other part C_d of the specific heat of the liquid at the same temperature which is caused by the cybotactic decomposition in raising the temperature by one degree is found by subtracting the value of C_m thus obtained from the observed value of the specific heat of the liquid at the temperature T_c. Hence by putting the values of y' and C_d thus found into equation (14) the heat of decomposition L_c of the cybotactic groups per one gram at the temperature T_c is obtained immediately. The values of L_c thus found for some values of ν and x_c are given in Tables II and III. The values of $(N_f/N)_c$ which are calculated with equation (11) for the same values of ν and x_c are also tabulated in the tables. By getting the values of x_c, L_c, $(C_f - C_c)_c$, $(N_f/N)_c$ and y' at the temperature T_c for a given value of ν in the above way, the values of L, x and consequently those of N_f/N, y' and C_d for any temperature T are calculated by means of equation (7), (10), (11), (13) and (14) for the same value of ν. The part C_m of the specific heat of the liquid at any temperature T which is required merely to raise the temperature by one degree of the free liquid molecules and the cybotactic groups without causing the cybotactic decomposition is then obtained by

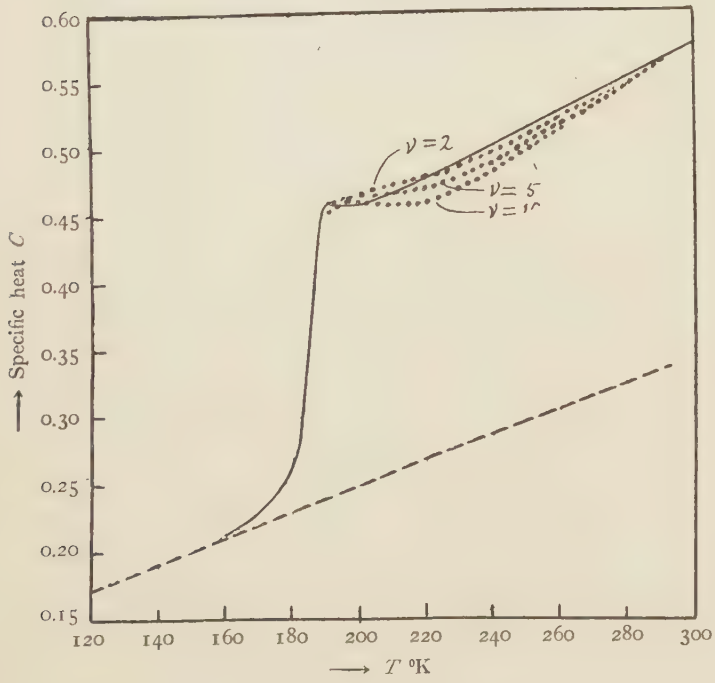
$$C_m = C_f\left(\frac{N_f}{N}\right) + C_c\left(1-\frac{N_f}{N}\right), \quad \text{.....(16)}$$

by using the values of N_f/N calculated as above and those of C_f and C_c at the same temperature. From the values of C_d and C_m calculated in the above way for various temperatures the actual values of the specific heat C of the liquid for various temperatures are thus obtained as the sum of C_m and C_d. In short, the essential point in calculating the specific heat of a super-cooled liquid lies in the choice of the values of ν and x_c, and this is done by repeated trials. The necessary data used for a few such trial calculations with glycerol are given in Table III, and the results of calculation for $\nu = 2$, 5 and 10 are shown in Fig. 3 by representing the calculated specific heat with dotted lines. When the values of x_c are smaller respectively than those given in Table III a hump comes about in the calculated specific heat curves at the temperatures just above T_c; and when they are larger the calculated specific

heat curves go down more rapidly with the rise of temperature than those shown in Figs. 3, 4, 5 and 6 respectively; and the values of x_c given in Tables II and III are so chosen that any noticeable hump does not appear in the calculated specific heat curve and that at the same time the shortage of the theoretical curve from the experimental one is smallest. The theoretical specific heat curves shown in Fig. 3, which are obtained for the case of $\nu=2$, 5 and 10 by using the values of x_c determined as above, indicate that the departure from the experimental curve decreases with the decrease of the value of ν, and that the agreement with the experimental curve becomes almost satisfactory with $\nu=2$. Thus, at the first sight, it seems to be reasonable to take 2 as an appropriate number of the constituent molecules of a cybotactic group. However, the specific heats of the free liquid molecules and of the cybotactic groups and the heat of decomposition of the cybotactic groups are determined approximately in a very rough manner. Moreover it is conceivable that many different kinds of cybotactic groups consisting of different numbers of molecules are present in a

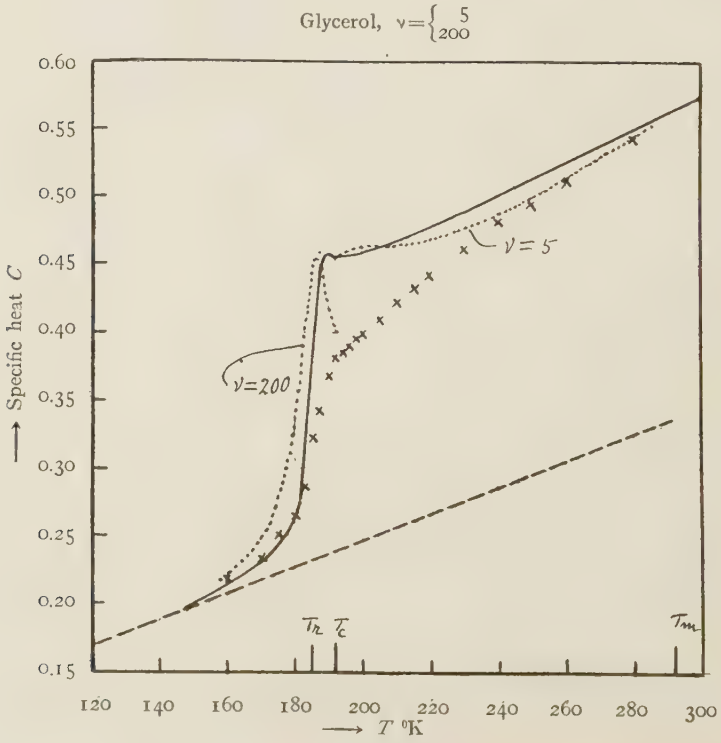
Fig. 3

Glycerol



super-cooled liquid. If we take these circumstances into consideration it seems appropriate to conclude, by leaving untouched on the definite number of the constituent molecules, that the general tendency of the specific heat of a super-cooled liquid can be explained by the presence in equilibrium of the free liquid molecules and the cybotactic groups each consisting of several molecules. Thus the writer provisionally took 5 as the number of constituent molecules of a cybotactic group in the case of the super-cooled state of glycerol, *dl*-lactic acid and ethyl alcohol; and the theoretical curves calculated with the data given in Table II are represented by dotted lines in Figs. 4, 5 and 6. General tendency of the theoretical curves is seen to be in accord with the experimental curves. In these figures the crosses represent the part C_m of the specific heat which is required merely to raise the temperature by one degree of the free liquid molecules and the cybotactic groups without causing the cybotactic decomposition; and the sum of C_m and C_a is taken as the theoretical specific heat C and is indicated by the dotted lines.

Fig. 4

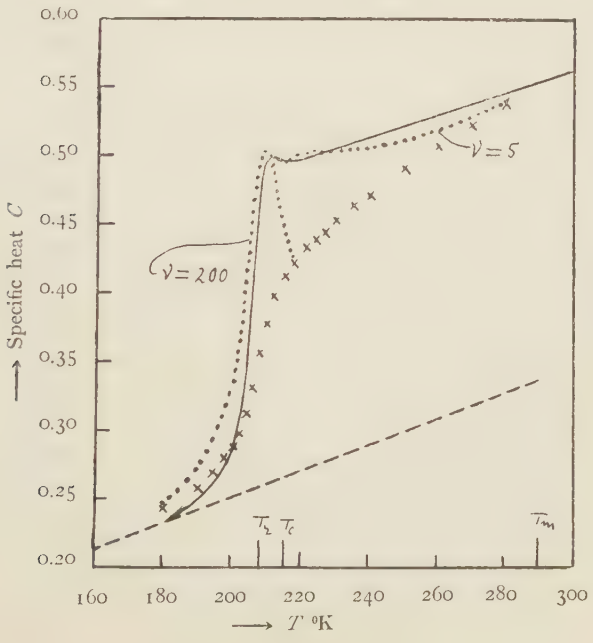


Structural Relaxation in the Softening Temperature Range

The writer considers the softening of an amorphous solid in its softening temperature range as the relaxation of the cybotactic structure, and the solidification of the super-cooled liquid into amorphous solid as the fixing of the cybotactic structure. Thus the solidification of the supercooled liquid can be considered as the fixing of the position of the free liquid molecules by means of the inter-molecular attraction whose effect becomes at low temperatures superior to that of the average kinetic energy of thermal motion of free molecules. Since the fixing of the position of the free molecules by intermolecular attraction signifies the formation of huge molecular aggregates composed of an immense number of molecules, entirely the same reasoning as in the case of the cybotactic equilibrium can be applied to this case. The increase of the specific heat in the softening temperature range is very sudden and this peculiarity seems to be accounted for by taking the number of constituent molecules of a huge molecular aggregate sufficiently great, as will be imagined from the shape of the y'-curve

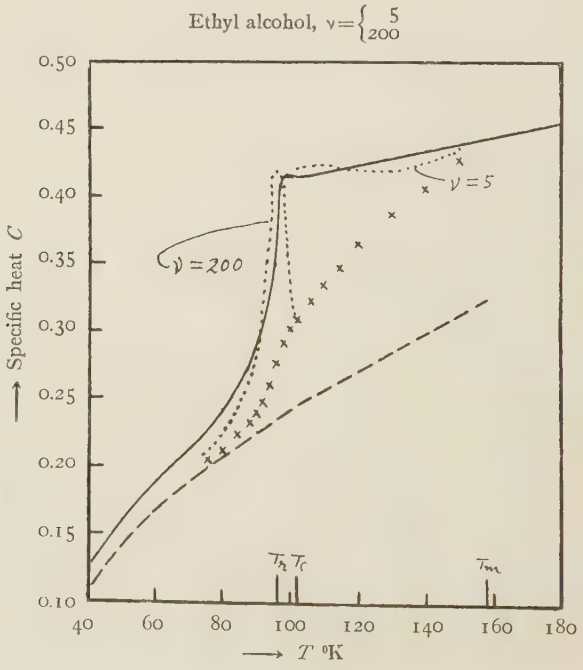
Fig. 5

dl-Lactic acid, $\nu = \begin{cases} 5 \\ 200 \end{cases}$



for a large number of ν as is shown in Fig. 2. Thus the writer provisionally took 200 as the number of constituent molecules of a huge molecular aggregate and an entirely similar calculation of the specific heat as in the super-cooled liquid state was made with glycerol, *dl*-lactic acid and ethyl alcohol. In carrying out the calculation, the writer assumed, for the sake of simplicity, that the amount of the cybotactic groups remained the same as at the temperature T_c, and that the huge molecular aggregates having 200 constituent molecules are formed only among the remaining free molecules so that only the relative proportion between the numbers of free molecules and of the huge molecular aggregates changes with temperature in equilibrium by keeping the amount of the cybotactic groups unaltered. As to the specific heats of the cybotactic groups and the huge molecular aggregates, the writer regarded them roughly to be the same as that of the adult crystal at the same temperature, and the specific heat of the still remaining free molecules was calculated by entirely the same assumption as in the case of the cybotactic equilibrium. As it is usual with an amorphous solid to be accompanied by some hysteresis in various physical pro-

Fig. 6



perties of it by changing the temperature in its softening range, it is meaningless to go into details in the present case where the equilibrium state is considered. Thus, in order to know only the general tendency of the temperature dependence of the specific heat, the writer disregarded the temperature variation of the heat of decomposition of the huge molecular aggregates and assumed it to be constant. In carrying out the actual calculation we must first select the reference temperature. The writer took the temperature at which the maximum of y' for $\nu=200$ occurs as such reference temperature and designated it to be very close to the temperature at which the sudden increase of the specific heat in the softening temperature range just ended. Such reference temperature is represented by T_r and its values for glycerol, *dl*-lactic acid and ethyl alcohol are tabulated in Table II together with the value of the degree of decomposition x_r of the huge molecular aggregates at these temperatures, which is so determined as to give the maximum value to y' for $\nu=200$. When the value of x_r is thus determined the corresponding value of N_f/N is obtained by equation (11), and the proportion of the number of the free molecules to the total number of molecules at the temperature T_r is found by multiplying this value of N_f/N with $(N_f/N)_c$ which is the proportion of the free molecules at the temperature T_c where the huge molecular aggregates decompose almost perfectly into the free molecules. Consequently the part C_m of the specific heat at T_r which is required to raise the temperature of the free molecules, the cybotactic groups and the huge molecular aggregates without causing the decomposition of the molecular aggregates is obtained from the values of the specific heats of the free molecules, of the cybotactic groups and of the huge molecular aggregates at the same temperature. Thus by knowing the value of C_m at T_r the other part of the specific heat C_d at the same temperature which is due to the decomposition of the huge molecular aggregates in raising the temperature is found immediately by subtracting the value of C_m from the observed specific heat at the temperature where the sudden increase of the specific heat in the softening range just ended. As the proportion of the total number of free molecules which can be transformed into the huge molecular aggregates is $(N_f/N)_c$, the value of C_d is obtained in the present case by multiplying with $(N_f/N)_c$ the equation (14), i. e.

$$C_d=\left(\frac{N_f}{N}\right)_c y'\frac{ML^2}{RT^2}, \quad \cdots\cdots(17)$$

The value L of the heat quantity which is necessary to decompose one gram of huge molecular aggregates is obtained by this equation, and the values thus found for glycerol, *dl*-lactic acid and ethyl alcohol are tabulated in Table II by being denoted by L_r. In this manner, essentially similar calculations of C_m, C_a and consequently C as in the case of cybotactic decomposition are performed for the case of decomposition of huge molecular aggregates, and the results are shown in Figs. 4, 5 and 6. In these figures the dotted lines represent the values of the specific heat C and the crosses represent the values of C_m which is required to raise the temperature merely by one degree of the free molecules, the cybotactic groups and the huge molecular aggregates without causing any decomposition. As is seen in the figures the value of C_a rises very rapidly with temperature to its maximum at T_r and then falls very rapidly almost to zero at T_c. The rapidity of the change of C_a with temperature can be still further improved by taking the number of constituent molecules of a molecular aggregate greater than 200. However, for the sake of understanding the general tendency of the change of specific heat with temperature it suffices with 200, and the results calculated for this case are plotted in the figures.

In calculating the specific heat by the structural relaxation the writer assumed, for the sake of simplicity, that the amount of the cybotactic groups remains unchanged at the temperatures below T_c. However, it will be somewhat different in actual case, and we can expect that the molecular exchange between the cybotactic groups and the free molecules still takes place to some degree in the temperature range from T_c to about T_r. Hence, if we assume that the gap found in the theoretical specific heat curve between T_c and T_r is filled in by this cause, the general tendency of the specific heat curve of an amorphous substance at the temperatures in and above its softening range is thus clearly understood.

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Two Theorems on the Connected Sets.

By

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Two point sets are said to be mutually separated if neither contains a point or limit point of the other. A set is said to be connected if it cannot be decomposed into two sets which are mutually separated.

[1]This note consists of two theorems on the connected sets:

I.[2] If M is a closed connected set, and if in M there is a largest division-set[3] A, then M is a simple arc.

II.[4] Let M be a closed connected set such that, if g is any connected subset of M, then $M-g$ consists of two components at most. Let the product of all division-sets of M not vanish, and let it be closed, then M consists of two simple closed curves which have a simple arc or a point in common.

Theorem I. If M is a closed connected set, and if in M there is a largest[5] division-set A, then M is a simple arc.

Proof.

Let $M-A=B+C$, where B is separated from C, then, $B+A$, as well as $C+A$, is connected. If $B=B_1+B_2$, where B_1 is separated from B_2, then $A+B_1$, as well as $A+B_2$, is connected. Then, $M-(A+B_1)=B_2+C$, where B_2 is separated from C, this contradicts to the fact that A is a largest division set. Hence B is connected. In the same way, C is also connected.

Now suppose B contains two points b_1 and b_2, then $B-b_1 \neq 0$. Let $B-b_1$ be connected, then, if $B-b_1$ is not separated from A, $M-$

1. In this paper we consider exclusively the euclidean space of any dimensions.

2. Concerning this theorem, confer C. Zarankiewicz "Sur les points de division dans les ensembles connexes", Fund. Math. IX. p. 143. Nevertherless, the author cannot agree to this Zarankiewicz's theorem.

3. If A is a connected subset of M such that $M-A$ is not connected, then A is called *a* division-set of M.

4. When $M-g$ is always connected, M is a simple closed curve. J. R. Kline "Closed connected sets etc.", Fund. Math. V. p. 3-10.

5. Any division set is contained in A.

$\{A+(B-b_1)\}=C+b_1$, which is a contradiction; if $B-b_1$ is separated from A, then b_1 is not separated from A and $M-(A+b_1)=C+(B-b_1)$, which is a contradiction. Hence $B-b_1=B_1+B_2$, where B_1 is separated from B_2. As B is connected, b_1+B_1, as well as b_1+B_2, is connected. As $A+B$ is connected, A is not separated from one of b_1+B_1 and b_1+B_2, say from b_1+B_1, then $A+b_1+B_1$ is connected, and $M-(A+b_1+B_1)=C+B_2$, which is a contradiction. Hence B consists of only one point b, in the same way C cosists of only one point c.

We say that M is a irreducible[1] connected set between b and c. Suppose any point p contained in $M-(b+c)$, then $M-c-p$ is not connected clearly. Let $M-c-p=D+E$, where D is separated from E, then since $M-c$ is connected, $p+D$ and $p+E$ are also connected. Let b be contained in D, then $D-b$ and E are mutually separated, and since $M-(b+c)$ is connected, $(D-b)+p$, as well as $p+E$, is connected. If c is not separated from D, $c+(D-b)+p$ is connected, and $M-\{c+p+(D-b)\}=b+E$, this is a contradiction. Hence c is separated from D. If c is separated from E, $M-(p+D)=c+E$, which is a contradiction.

Therefore, $M-p=D+(E+c)$, where D is separated from $E+c$, and $b\in D$, $c\in E+c$.

Now, let P be any connected set contained in M, containing neither b nor c, and let p be any point contained in P. $M-p=H+K$, where H is separated from K, and where $b\in H$, $c\in K$. $M-P=(H-P)+(K-P)$, where $b\in H-P$ and $c\in K-P$, and where $H-P$ is separated from $K-P$.

Now, suppose N to be any connected set contained in M, containing b and c. If $M-N$ is not equal to zero, then,[2] let P be any component of $M-N$, $M-P$ is connected. On the other hand, as P contains neither b nor c, $M-P$ is not connected. Hence $M=N$, that is, M is a closed irreducible connected set between b and c. Therefore M is a simple arc.

Q. E. D.

Theorem II. Let M be a closed connected set such that, if g is any connected subset of M, then $M-g$ consists of two components at most. Let the product of all division sets of M not vanish, and

1. There is no connected subset of M which is different from M and contains b and c. cf. B. Knaster and C. Kuratowski "Sur les ensembles connexes" Fund. Math. 11. p. 214.
2. cf. "Sur les ensembles connexes" Fund, Math. 11. p. 214.

let it be closed, then M consists of two simple closed curves which have a simple arc or a point in common.

Proof. Let A be the product of all division sets, and let B be its complement with respect to M.

In the first place we say that B should not consist of more than three components. If B has more than three components, then A should not be connected clearly. Suppose now a connected subset C containing A such that $M-C$ has two components.

$M-C$ contains points of two components of B at most, which may be written B_1 and B_2, where it is possible that $B_1=B_2$. Let us denote $(M-C)B_1=B_1'$ and $(M-C)B_2=B_2'$. Let B_3 be a component of B, where $B_3\neq B_1$ and $B_3\neq B_2$, then $C-B_3$ is not connected.

Consequently $C-B_3$ can be decomposed in the following form. $C-B_3=T+S$, where T is separated from S. Now, B_1', as well as B_2', must be separated from neither T nor S. If B_1' were separted from T or S, say from T, and B_2' were separated from T or S, say from T, then $M-B_3=B_1'+B_2'+T+S=(B_1'+B_2'+S)+T$, which is a contradiction. Hence one of B_1' and B_2', say B_1', is separated from neither T nor S. If B_2' is separated from T, then $M-(B_1'+B_3+S)=B_2'+T$. If $T\cdot A=0$, then, as $M-(B_1'+S+B_3+B_2')=T$, T contains the points of two components of B at most, from this T is separated from B_3, which is a contradicton. Hence $T\cdot A\neq 0$ and so $M-(B_1'+B_3+S)$ is connected, this is contradiction. Therefore, B_1', as well as B_2', is separated from neither T nor S. From this, after a short consideration, $A\cdot T\neq 0$ $A\cdot S\neq 0$, and so T and S are both connected. Next, we remove B_4 from C, where $B_4\neq B_1$, $B_4\neq B_2$, $B_4\neq B_3$, and where B_4 is a component of B, then $C-B_4$ is not connected, Let us denote $C-B_4=T'+S'$, where T' is separated from S'. B_4 is contained in T or S entirely, say in T, then B_3+S is contained in $C-B_4$. B_3+S is connected, B_3+S is contained in one of T' and S', say in S', entirely. Let us denote $S'-(B_3+S)=T_1$, $T'=T_2$. $S'+B_4$ is connected, and B_4 is separated from $S+B_3$, so $T_1\neq 0$. We could say that $A\cdot T\neq 0$ $A\cdot S\neq 0$, and T and S are both connected. In the same way, $A\cdot T'\neq 0$ $A\cdot S'\neq 0$, and T' and S' are both connected. $A\cdot T_1\neq 0$. Because, if $T_1\cdot A=0$, then $M-(B_4+T_2+B_1'+S+B_3+B_2')=T_1$ contains the points of two components of B at most, so T_1 is separated from B_3+S, which is a contradiction to the fact that T_1+B_3+S is connected. Now suppose that T_1 is separated from B_2', then $M-(T_2+B_4+B_1'+S+B_3)=T_1+B_2'$, whereas T_1 contains points of A, this

is impossible. $T_1+B_4+T_2=T$, which is a connected set. T_1 and T_2 are mutually separated, so T_1+B_4 is connected. T_1 is not separated from B_2', and $B_4+T_1+B_2'+S+B_1'$ is connected, so $M-(B_4+T_1+B_2'+S+B_1')=T_2+B_3$, whereas T_2 contains points of A, which is a contradiction. After all, B should consist of three components at most. Suppose now $B=B_1+B_2+B_3$, where B_1, B_2, B_3 are three components of B, then A is not connected, so $A=A_1+A_2$, where A_1 is separated from A_2. At least two components among B_1, B_2, B_3 are separated from neither A_1 nor A_2, say, B_1 and B_2 are separatod from neither A_1 nor A_2. Suppose that B_3 is separated from A_2 and not separated from A_1, then $A_2=M-(B_1+A_1+B_2+B_3)$ is connected. For $M-B_1=B_2+A_1+B_3+A_2$ is connected, and $M-(B_1+B_2)=(A_1+B_3)+A_2$, where A_1+B_3 is separated from A_2, and so $A_1+B_3+B_2$ is connected. A_1 cannot be connected, so $A_1=A_1'+A_2'$, where A_1' is separared from A_2'. As A_1+B_3 is connected, $A_1'+B_3$, as well as $A_2'+B_3$, is connected. A_1' and A_2' cannot be separated from one of B_1 and B_2. Let A_1' be not separated from B_1, then $A_2'=M-(A_1'+B_1+B_2+B_3+A_2)$ is connected, and in the same way A_1' is connected. Clearly A_1' is separated from B_2, and A_2' is separated from B_1. In the next place, suppose that B_1, B_2 and B_3 are separated from neither A_1 nor A_2. Let $M-(B_1+B_2)$ be connected, then A_1 and A_2 are both connected. Let $M-(B_1+B_2)$ be not connected, then we can write $A_1+A_2+B_3=(B_3+A_1')+A_2'$, where $A_1+A_2=A_1'+A_2'$, and where B_3+A_1' and A_2' are mutually separated. In this case, B_1 and B_2 are separated from neither A_1' nor A_2', and B_3 is separated from A_2', so $A_1'+A_2'=A_1+A_2=A$ consists of three components.

If B consists of two components, then, after a short consideration A consists of two components at most.

Consequently the following five cases can arise:

1) A is a connected set, and B is also a connected set.
2) A is a connected set, and B consists of two components.
3) A consists of two components, and B consists of two components.
4) A consists of two components, and B consists of three components.
5) A consists of three components, and B consists of three components.

In the first place let us consider the case 2).

Let $M-A=C+D$, where C and D are components of B, then

$A+C$ and $A+D$ are connected. If E be any connected set contained in $A+C$, the following five cases may arise:

i. E is contained in C.

ii. E is contained in A.

iii. E contains C, and yet $E\cdot A$ is not zero.

iv. E contains A, and yet $E\cdot C$ is not zero.

v. $E\cdot C$, $E\cdot A$, $A-E$, and $C-E$ are not zero.

Let us first consider the case i), Suppose $(A+C)-E=F+G$, where F is separated from G, then, as A is connected, A is contained in one of F and G entirely, say in F, and so G is contained in C. Hence G is separated from D. From this, $F+D$ is separated from G. $M-E=(A+C+D)-E=(D+F)+G$, whereas E contains no point of A, which is a contradiction. Hence $(A+C)-E$ is connected.

ii) If $E=A$, then $(A+C)-E=C$, which is connected. Suppose $A-E$ is not zero. If E were separated from D, then, as $M-\{(A+C)-E\}=D+E$, $(A+C)-E$ is not connected. Hence $(A+C)-E=F+G$, where F is separated from G. As C is connected, C is contained in one of F and G, say in F, so G is contained in $A-E$. $E+F$ and $E+G$ are both connected. As $M-E=D+F+G$, $D+F$ and $D+G$ are both connected. If $C=F$, then $G=A-E$ and $M-E=(A-E)+D+C$, where C is separated from $(A-E)+D$; this is a contradiction. Therefore $F-C$ is not zero. $A-E=(F-C)+G$, where $F-C$ is separated from G. $M-\{E+(F-C)\}=C+(G+D)$, where C is separated from $G+D$. On the other hand, G is contained in A, which is a contradiction. Therefore E should not be separated from D, and $(A+C)-E=M-(D+E)$, which is connected.

iii) As $E\cdot A$ is not zero, E is not separated from D, and $(A+C)-E=M-(E+D)$, which is connected.

iv) E contains A, $(A+C)-E$ is connected clearly.

v) As $E\cdot A$ is not zero, E is not separated from D. $(A+C)-E=M-(E+D)$. As $A-E$ is not zero, $(A+C)-E$ is connected.

Therefore $A+C$ is a closed connected set such that, if E is any connected subset of $A+C$, then $(A+C)-E$ is also connected. As $A+C$ contains more than one point, by Kline's theorem, $A+C$ is a simple closed curve. In the same way $A+D$ is a simple closed curve. A is a simple arc or one point. In the case 2), A should not be a simple arc. Therefore M consists of two simple closed curves which have one point in common. Conversely such M satisfies the condition of theorem II clearly.

Now let us consider the case 3) and let $M=A+B$, $A=A_1+B_1$, $B=C_1+D_1$, where A_1 and B_1 are components of A, and C_1 and D_1 are components of B. Clearly A_1 is separated from neither C_1 nor D_1; B_1 is also unseparated in the same way. Let D_2 be a set of limit points of D_1, contained in A_1. If D_2 contains two points a and b, then $A_1-(a+b)=M-\{D_1+a+b+B_1+C_1\}$ is connected, and $A_1-(a+b)$ is not separated from C_1. So $M-\{A-(a+b)+C_1+B_1+D_1\}=a+b$, which is impossible. Hence D_2 consists of only one point d_2, and by the same reason, a set of limit points of C_1 contained in A consists of one point c_2. When c_2 is coincident with d_2, A_1 is coincident with d_2 clearly. When c_2 is not coincident with d_2, A_1 is a irreducible cennected set between d_2 and c_2, that is, a simple arc. Let c_3 be a limit point of C_1 contained in B_1, and let d_3 be a limit point of D_1 contained in B_1. B_1 is a point c_3 or a simple arc of which extremties are c_3 and d_3. $C_1+c_2+c_3$ is clearly closed connected set, and let E be any connected subset of $C_1+c_2+c_3$, which contains only one point of c_2 and c_3, say c_2, then $C_1+c_2+c_3-E$ is a connected set, because $M-\{E+A_1+D_1+(B_1-c_3)\}=C_1+c_2+c_3-E$. If[1] E contains both c_2 and c_3, then $C_1+c_2+c_3-E$ is connected, because $M-E=(C_1+c_2+c_3-E)+\{D_1+(A_1-c_2)+(B_1-c_3)\}$, and yet $C_1+c_2+c_3-E$ is separated from $D_1+(A_1-c_2)+(B_1-c_3)$. Therefore $C_1+c_2+c_3$ is a closed connected set containing a largest division set C_1, so by theorem I, $C_1+c_2+c_3$ is a simple arc, of which extremities are c_2 and c_3. In the same way, $D_1+d_2+d_3$ is also a simple arc. Hence M should be a simple closed curve, whereas the simple closed curve does not satisfy the condition of theorem II. Therefore the case 3) can not arise.

Let us now consider the case 4), and let $M=A+B$, $A=A_1+B_1$, $B=C_1+D_1+E_1$, where A_1 and B_1 are components of A, and C_1, D_1 and E_1 are components of B. B_1, as well as A_1, is not separated from C_1, D_1 and E_1 clearly. Suppose any connected set G contained in B_1. If G is not separated from one of C_1, D_1 and E_1, say from C_1, then $B_1-G=M-(G+C_1+D_1+E_1+A_1)$ is connected. Next, let G be separated from C_1, D_1 and E_1. In this case, if B_1-G is not connected, then $B_1-G=T+S$, where T is separated from S. Suppose that T is separated from C_1 and yet S is not separated from one of D_1 and E_1, then $M-(S+G+D_1+A_1+E_1)=C_1+T$; on the other

1. When $A_1=c_2$ and $B_1=c_3$, we cannot directly say that $C_1+c_2+c_3-E$ is zero.
When A_1 is not equal to c_2 or B_1 is not equal to c_3, it goes without saying that $C_1+c_2+c_3-E$ is zero.

hand, $S+G+D_1+A_1+E_1$ does not entirely contain A, which is a contradiction. Hence, if T is separated from C_1, then S is separated from D_1 and E_1. As S is separated from D_1 and E_1, T is separated from C_1, D_1, and E_1. Hence $B_1=G+S+T$ is separated from D_1; this is impossible. T, as well as S, is not separated from C_1, D_1 and E_1. $M-(T+G+C_1+D_1+E_1)=S+A_1$, which is impossible. Hence B_1 is a closed connected set such that, if E is any connected subset of B_1, B_1-E is also connected. Hence B_1 is one point or a simple closed curve. Suppose that B_1 is a simple closed curve. In this case, let c_1, d_1, e_1 be a point of a set of limit points of C_1, D_1, E_1 respectively, contained in B_1, then $M-(C_1+D_1+E_1+\widehat{c_1d_1e_1})=A_1+(B_1-\widehat{c_1d_1e_1})$, where $\widehat{c_1d_1e_1}$ is a simple arc contained in B_1, which contains c_1, d_1, e_1 and of which extremities are c_1 and e_1. $\widehat{c_1d_1e_1}+C_1+D_1+E_1$ does not entirely contain A, and yet its complement with respect to M consists of two components; which is impossible. Therefore B_1 consists of only one point b_1, and, in the same way, A_1 consists of only one point a_1. $b_1+a_1+C_1$ is a closed and irreducible connected set between b_1 and a_1, that is, $b_1+a_1+C_1$ is a simple arc. $b_1+a_1+D_1$ and $b_1+a_1+E_1$ are also simple arcs. Hence M consists of two simple closed curves which have a simple arc in common. Conversely such M suffices the condition of theorem II.

Let us now consider the case 5) and let $A=A_1+B_1+C_1$, $B=D_1+E_1+F_1$, where A_1, B_1 and C_1 are components of A, and D_1, E_1 and F_1 are components of B. After a short consideration, D_1 is not separated from two of A_1, B_1 and C_1, and is separated from the other one. It is the same for E_1 and F_1. We may suppose that D_1 is not separated from both A_1 and B_1, and is separated from C_1, and that E_1 is not separated from both A_1 and C_1, and is separated from B_1, and that F_1 is not separated from both B_1 and C_1, and is separated from A_1. A set of limit points of D_1, contained in A_1, consists of only one point d_1, and a set of limit points of E_1, contained in A_1, consists of only one point e_1. If d_1 is coincident with e_1, then A_1 consists of only one point d_1. If d_1 is not coincident with e_1, then A_1 is an irreducible connected set between d_1 and e_1. Hence A_1 is one point or a simple arc, as B_1 and C_1 also are. By the same reason as with the case 3), M is a simple closed curve, whereas a simple closed curve does not suffice the condition of theorem II. Therefore case 5) cannot arise.

Now, let us consider the case 1). A set of limit points of B,

contained in A, consists of only one point. If it consists of two points c and d, then A is clearly irreducible between c and d, and so is $B+c+d$ also. Hence M is a simple closed curve, which is impossible. If a set of limit points of B, contained in A, contains three points c, d and e, then $M-(B+c+d)=A-(c+d)$, which is connected. $M-[B+\{A-(c+d)\}]=c+d$: this is a contradiction. Hence a set of limit points of B, contained in A, consists of only one point a. $M-a=B+(A-a)$: hence A is coincident with the point a. Suppose a set C, where $C+a$ is connected, such that $M-(C+a)$ consists of two components. If we choose an adequate C, then C may be supposed connected. Suppose it were impossible. Let $M-(a+C)=E+F$, where E is separated from F, then $C=C_1+C_2$, where C_1 is separated from C_2. $E+F+C_1+C_2=B$ is connected, so at least one of E and F, say F, is separated from neither C_1 nor C_2. Suppose that E is separated from C_2, and that it is not separated from C_1. If $C_2=C_2'+C_2''$, where C_2' is separated from C_2'', then C_2' and C_2'' are connected. F is not separated from one of C_2' and C_2'', say C_2', then $M-(C_2'+F+a)=C_2''+(C_1+E)$. On the other hand, $C_2'+F$ is connected, and C_2'' is separated from C_1+E. This is a contradiction. Hence C_2 is connected. In the same way, C_1 is connected. Now as C_1+F is connected, $M-(C_1+F+a)=E+C_2$, which is a contradiction. Hence E, as well as F, is not separated from both C_1 and C_2. In this case, if one of C_1 and C_2 is not connected, then the other is also not connected. Suppose that $C_1=C_1'+C_1''$, where C_1' and C_1'' are two components of C_1, and that $C_2=C_2'+C_2''$, where C_2' and C_2'' are two components of C_2. One of C_1' and C_1'' is separated from E and not from F, and the other is separated from F and not from E. Let C_1' be separated from F, and let C_1'' be separated from E. In the same way, let C_2' be separated from F and let C_2'' be separated from E. $C_1'+C_2'$ is separated from $C_1''+C_2''$ and yet $C_1'+C_2'$ is separated from F, which is impossible. Hence C_1 and C_2 are both connected sets. E, as well as F, is clearly not separated from the point a. Let e_1 be a limit point of E, contained in C_1, then C_1-e_1 is a connected set. If e_1 is a limit point of F, then $E+F+e_1$ is connected, and $M-(E+F+e_1+a)=(C_1-e_1)+C_2$, which is impossible. If e_1 is not a limit point of F, then $(C_1-e_1)+F+C_2+E$ is connected, and $M-\{(C_1-e)+F+C_2+E\}=a+e_1$, which is impossible. Hence there is no limit points of E contained in C_1. In the same way, there is no limit points of C_1 contained in E. This contradicts to the fact that C_1 is not separated from E.

Therefore we may choose an adequate connected set C such that $M-(C+a)=E+F$, where E is separated from F. As $M-C=E+a+F$, which is connected, it is clear that $E+a$ and $F+a$ are both connected. A set of limit points of C contained in F consists of only one point at most. If it contains two points f_1 and f_2, then $F-f_1$, as well as $F-f_2$, is connected. $(F-f_1)+C+E$ is connected, and $M-\{(F-f_1)+C+E\}=f_1+a$, which is a contradiction. In the same way, a set of limit points of C contained in E consists of only one point at most. We put these points in C, then we may consider $M-(C_1+a)=E_1+F_1$, where C_1 is connected, and where E_1 is separated from F_1 and $\overline{C_1}$[1]$(E_1+F_1)=0$. A set of limit points of E_1, contained in C_1, consists of one point. If it contains two points e_1 and e_2, then $(E_1+e_1+e_2)+a+F_1$ is connected. $M-\{(E_1+e_1+e_2)+a+F_1\}=C_1-e_1-e_2$, and this consists of two components at most. Suppose that $C_1-e_1-e_2=C_2+C_3$, where C_2 is separated from C_3, then at least one of $C_2+e_1+C_3$ and $C_2+e_2+C_3$, say $C_2+e_2+C_3$, is connected. $M-(E_1+e_1+e_2+a)=C_2+C_3+F_1$, and so F_1 is not separated from one of C_2 and C_3, say from C_2, then $M-(E_1+e_2+C_2+C_3+F_1)=e_1+a$, which is a contradiction. Hence $C_1-e_1-e_2$ must be connected. If F_1 is separated from $C_1-e_1-e_2$, then F_1 is not separated from one of e_1 and e_2, say e_1, so $M-\{F_1+E_1+e_1+(C_1-e_1-e_2)\}=e_2+a$, which is a contradiction. F_1 is not separated from $C_1-e_1-e_2$, so $M-\{F_1+(C_1-e_1-e_2)+e_1+E_1\}=e_2+a$, which is impossible. Therefore a set of limit points of E_1, contained in C_1, consists of one point e_1. In the same way a set of limit points of F_1, contained in C_1, consists of one point f_1.

$a+E_1+e_1$ is clearly a closed connected set, and let G be any connected subset of $a+E_1+e_1$, where G contains at least one of a and e_1, then $(a+E_1+e_1)-G$ is connected. Hence $a+F_1+e_1$ is a simple arc, of which extremities are a and e_1. In the same way, $a+F_1+f_1$ is a simple arc, of which extremities are a and f_1. If e_1 is coincident with f_1, then C_1+a is a simple arc, of which extremities are a and f_1. Hence M consists of two simple closed curves which have a simple arc in common. This is impossible in case 1). Therefore e_1 is not coincident with f_1. A proper connected subset of C_1+a clearly does not simultaneously contain a, e_1 and f_1. Let H be a connected subset ef C_1+a, which contains two of a, f_1 and e_1 simultaneously and does not contain the other one, then a complement of H with respect to C_1+

1. $\overline{C_1}$ denotes a closure of C_1.

a is connected. Let H be a connected subset of C_1+a, which contains e_1 and does not contain f_1 and a, then $(C_1+a)-H$ consists of two components at most. Let $(C_1+a)-H=G+K$, where G is separated from K, and where $a \in G$ and $f_1 \in K$. $G=M-(K+F_1+H+E_1)$, so G is connected. As any proper connected subset of C_1+a cannot simultaneously contain f_1, a, e_1, K is connected. Let H be a connected subset of C_1+a, which contains f_1 and does not contain e_1 and a, then $(C_1+a)-H$ consists of two components at most. Let H be a connected subset of C_1+a, which contains a and does not contain e_1 and f_1, then $(C_1+a)-H$ consists of two components at most. Let H be a connected subset of C_1+a, which does not contain a, e_1 and f_1, then $(C_1+a)-H$ consists of three components at most.

Therefore C_1+a does not contain a[1] continuum of condensation, so[2] C_1+a is a Jordan continuum. Hence[3] a can be joined with e_1 by a simple arc $\overset{\frown}{ae_1}$ contained in C_1+a, where the extremities of $\overset{\frown}{ae_1}$ are a and e_1. In the same way a can be joined with f_1 by a simple arc $\overset{\frown}{af_1}$ contained in C_1+a, where the extremities of $\overset{\frown}{af_1}$ are a and f_1. It is clear that $C_1+a=\overset{\frown}{ae_1}+\overset{\frown}{af_1}$. $M=\overset{\frown}{ae_1}+\overset{\frown}{af_1}+(a+E_1+e_1)+(a+F_1+f_1)$, which is impossible in case 1). Therefore 1) cannot arise.

Q. E. D.

In conclusion the author wishes to express his hearty thanks to Professor T. Matsumoto for his kind advice.

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1. A set g is said to be a continuum of condensation of a set M, if g is a closed connected subset of M containing more than one point such that every point of g is a limit point of $M-g$. Suppose a connected set M such that, if N is any division set of M, $M-N$ consists of three components at most, then M does not contain a continnum of condensation. We can prove this easily.

2. Cf. S. Mazurkiewicz "Sur les lignes de Jordan" Fund. Math. 1. p. 176.

3. Cf. Moore "A theorem concerning continuous curves" Bull. Amer. Soc., Vol. 23 (1917). S. Mazurkiewicz "Sur les lignes de Jordan".

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